INVESTIGATIONS IN THE CHEMISTRY OF GUTTA-PERCHA AND BALATA.

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by

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I N D E X.

Introductory.

Experimental.

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I N T R O D U C T O R Y.

GUTTA-PERCHA and BALATA.

Sources.

Gutta-percha.

This is the name applied to the evaporated milky fluid or latex furnished by several trees found chiefly in the Malay Archipelago. The best gutta-percha is got from trees belonging to the family Sapotaceae, such as Palaquim oblongifolia, Dichopsis gutta, and others, while inferior products are yielded by allied trees of the same genus, chief among them being a species of Payena. Gutta-percha yielding trees are almost entirely confined to the Malay Peninsula and its immediate neighbourhood.

The latex is a greyish milky fluid chiefly secreted in cylindrical cells in the cortex layer of the tree. Latex occurs also in the leaves and may be removed by powdering them and extracting with an appropriate solvent. Indeed, de Jong (Rec. Trav. Chim., 50, 1018, 1931) has recently stated that the best method for obtaining the pure hydrocarbon is the extraction of the leaves with light petroleum. In order to collect the latex from the trees, incisions are made through the bark and from these it flows slowly, not nearly so freely as does rubber latex. On this account the trees are often felled, the branches chopped off and channels cut in the bark. The latex fills these channels, is then removed and converted

into gutta by boiling in open vessels over wood fires, the work usually being carried on in the wet season when the latex is more fluid and more abundant.

Gutta-percha appears in commerce in the form of blocks or cakes, and flocks of a dirty greyish appearance. The material is just soft enough to be indented by the nail: it has a fibrous structure and unlike rubber is almost completely inelastic. It possesses the unique property of becoming soft and plastic on immersion in hot water and hardening again on cooling without becoming brittle. It can be moulded or rolled in the plastic state and retains the desired shape on cooling. Rubber, on the other hand, to which substance both gutta-percha and balata are related by botanical origin and otherwise, when treated in this manner becomes sticky and slightly plastic, but it retains its resiliency.

Balata.

This valuable raw material resembling gutta-percha very closely, and the best natural substitute for it, is the product obtained by coagulating the latex of the so-called "bullet tree" (Mimusops globosa), a very close relative of the gutta-percha tree. It belongs to the same botanical family, the Sapotaceae, and is native to the West Indies, Guiana, Venezuela and Brazil.

Originally the tree was felled before collection of the latex, now, however, owing to the danger of wiping out the species, the latex is obtained by the method of periodical tapping. After collection the latex is transferred to shallow wooden vessels in which it is exposed to the air until coagulation has been brought about by the heat of the sun. By this means balata is obtained in sheets of about the same hardness as gutta-percha and often reddish in colour. Coagulation of the latex is often induced by boiling as in the case of gutta-percha, but never by the acid process — addition of acid to the watery latex — commonly employed to coagulate rubber latex.

Balata resembles gutta-percha very closely. It is an inelastic solid like the latter, and when immersed in hot water it behaves in the same manner, becoming soft and plastic and hardening on cooling without becoming brittle.

Purification of the Hydrocarbons.

Crude gutta-percha and balata consist mainly of a hydrocarbon with which occurs a quantity of dirt and foreign material and varying percentage of resins. These are separated by a modification of Harries' method for the purification of caoutchouc - this is the name used by the Chemical Society to denote the hydrocarbon constituent of rubber.

(Untersuchungen über Kautschukarten, p.7, Berlin, 1919).

The raw material is dissolved in hot petroleum ether and kept at about 40°C until the dirt has settled, leaving a clear solution above (Mair and Todd, J.C.S., 1932, p.393). On cooling to room temperature the hydrocarbon comes out of solution as a white pasty mass; this is separated mechanically from the dirty material and filtered free from absorbed solvent. The resins remain in solution, being much more soluble in petroleum ether than the hydrocarbon and so a separation is effected. This operation is carried out four or five times until all the dirt is got rid of and all the resins dissolved out. Finally the warm solution is run into a large volume of acetone. This precipitates the hydrocarbon, gutta-percha or balata in beautiful white flakes: these are filtered and refluxed in absolute alcohol for a few hours; and this coagulates the hydrocarbon into a transparent white lump. This is again dissolved in petroleum ether, precipitated with acetone and refluxed in alcohol. Finally the product is dried in a vacuum desiccator and stored in a coloured bottle in an atmosphere of carbon dioxide. The hydrocarbon thus purified gives the empirical formula (C_5H_8) on analysis.

The resins are somewhat complex mixtures and thus, although a few investigators have worked on them, they have

not yet been fully characterised. Payen in 1852 separated the resins of gutta-percha into two fractions, (1) a white crystalline substance soluble in hot alcohol, (2) a yellow amorphous substance insoluble in alcohol. These he named Alban and Fluavil respectively. Oesterle (Arch. Pharm., 230, 641, 1892) isolated an unstable substance which he named Guttan, and Tschirch (Arch. Pharm., 241, 481, 1903) separated the alban fraction into spherite-alban, $C_{30}H_{44}O_2$, M.P. 152°C, and crystal-alban, $C_{60}H_{80}O_3$, M.P. 228°C. It was later shown that crystal-alban was an ester of cinnamic acid and lupeol, (van Romburgh, Ber., 37, 3440, 1904).

Balata resins are analogous to those of gutta-percha and consist of (1) Balaban, and (2) Balafluavil. Tschirch and Schereschewscki (Arch. Pharm., 243, 358, 1905) further separated the balalban fraction into α-balalban, $C_{27}H_{42}O_2$, M.P. 230 - 231°C, and β-balalban, $C_{27}H_{44}O_2$ or $C_{27}H_{46}O_2$, M.P. 108 - 109°C. Two years later Cohen (Arch. Pharm., 245, 245, 1907) showed that α-balalban was identical with β-amyrin acetate.

Other and better methods than Harries' (above) have been devised for the purification of caoutchouc. Caspari (J.S.C.I., 32, 1041, 1913), by allowing acetone extracted caoutchouc to diffuse in ether, obtained an ether soluble and insoluble, fractions which have since been named

sol- and gel-caoutchouc by Pummerer and Pahl (Ber., 60, 2152, 1927). This has been confirmed in an unexpected manner by the work of Bruson, Sebrell and Calvert (Ind. Eng. Chem., 19, 1033, 1927) which will be referred to later (p.80). Fisher, however, has thrown some doubt on this, stating that on continuous extraction gel-caoutchouc slowly dissolves in ether (Chem. Rev., 7, 65, 1930), and Staudinger (Ann., 488, 153, 1931) states that the sol may change into the gel form and vice versâ. Experiment shows little difference between sol- and gel-caoutchouc. Pummerer and Mann (Ber., 62, 2636, 1929) found almost identical oxygen and iodine numbers for the two fractions, and Staudinger and Bondy (Ber., 63, 734, 1930) found the molecular weights for the sol and gel fractions to be 5200 and 7300 respectively, so that the difference seems to be one of degree of polymerisation. Fractional precipitation methods have also been used to advantage in removing the last traces of nitrogen due to the protein network which is present in caoutchouc. These methods are reported to deal effectively with this difficulty and have been perfected by Pummerer and his co-workers (Ann., 438, 295, 1924; Ber., 60, 2148, 1927; Ber., 61, 1583, 1928).

These specialised methods have not been applied extensively to gutta-percha and balata. These substances do not show a separation into sol and gel forms, and furthermore they have no protein network. Staudinger and

Bondy (Ber., 63, 724, 1930) have fractionated balata into five fractions by cooling benzene, toluene, or xylene solutions. From viscosity measurements these fractions appear to be different polymerisation grades and this fractionation might be interpreted as a partial separation of balata into some grades of the great number of polymers, of which, it is becoming more evident, the three hydrocarbons, gutta-percha, balata, and caoutchouc are made up.

Physical Properties.

The purified hydrocarbons are tough, white, amorphous solids, retaining in an enhanced degree the thermoplasticity of the crude materials. They are soluble in carbon tetrachloride, benzene, chloroform, and petroleum ether to give colloidal solutions, the nature of which is discussed by Staudinger (Ber., 63, 921, 1930), and insoluble in alcohol, acetone and acetic acid. The density of the hydrocarbons is about 0·940 and the heats of combustion found by Messenger (Trans. Inst. Rubb. Ind., 5, 71, 1929) are 10,990 and 11,000 calories/gm. for gutta-percha and balata respectively, thus showing close similarity between the substances.

The molecular weights are not easily determined since these hydrocarbons do not depress the freezing point of benzene, and the heating in camphor in the Rast method leads

to decomposition and incorrect molecular weights (Staudinger, Ber., 61, 2575, 1928). From viscosity measurements the values 50,000 and 51,000 for the molecular weights of gutta-percha and balata were found by Staudinger (Ann., 488, 1, 1929; Ber., 63, 921, 1930). These values, although perhaps inexact, serve to demonstrate the order of magnitude of the molecular weights.

Röntgenographic examination of the hydrocarbons shows a crystalline structure with a transition from an α to a β form between 65 - 75°C. This is now well established from the observations of Hopff and von Susich (Kautschuk, 6, 234, 1930); Hauser and von Susich (K., 7, 120, 1931); and Stillwell and Clark (K., 7, 86, 1931). Both gutta-percha and balata are crystalline in the unstretched state, and Hopff and von Susich state that balata hydrocarbon is röntgenographically identical with gutta-percha hydrocarbon. Stillwell and Clark, however, doubt this and so nothing definite can yet be stated. Kirchoff (K., 5, 175, 1929) found the specific gravity of crystalline balata to be 0·9571.

Chemical Properties.

The chemical properties of these hydrocarbons depend mainly on the fact that they are unsaturated, thus their chief chemical reaction is addition, and study of the

addition products leads to the conclusion that there is one double bond present for each C_5H_8 group. These addition products are all amorphous substances of extremely high molecular weight, the soluble ones giving colloidal solutions. Since none of these substances is crystalline or can be distilled without decomposition, their purification is somewhat difficult. When pure, however, they give constant analysis and so the hydrocarbons are assumed to be chemical individuals, or complexes acting as such.

Saturation of the double bonds does not reduce the size of the polymer to anything of even reasonable weight, e.g., 50,000 is the molecular weight found by Staudinger and Leupold (Helv. C.A., 15, 221, 1932) for hydro-balata, and the bromides of gutta-percha and balata, like the hydrocarbons, do not depress the freezing point of benzene. While gutta-percha and balata seem to be very similar, this similarity is accentuated almost to identity in the saturated derivatives: thus Staudinger (K., p.9, 1925) found the same refractive index for the hydrogenation products of caoutchouc, gutta-percha and balata, and Mair and Todd (J.C.S., 393, 1932) found a compound, $C_{56}H_{88}O_{28}$, alcoholic in character, to be a common oxidation product. Thus similar derivatives of gutta-percha and balata are considered to be almost identical.

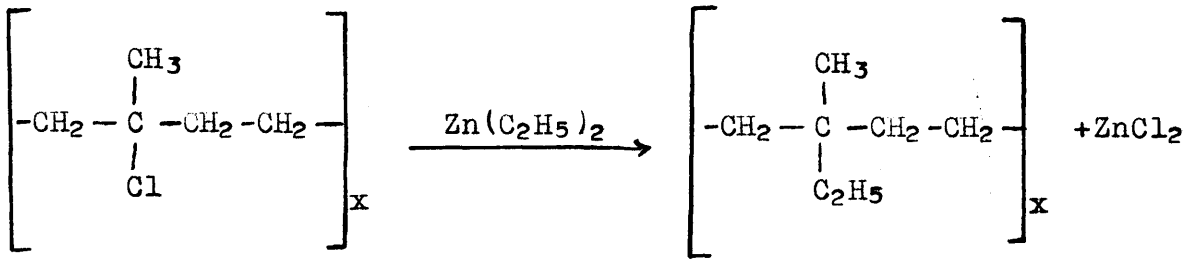
Action of Halogens.

Early work on the addition of chlorine to caoutchouc led to the conclusion that substitution as well as addition takes place, thus Gladstone and Hibbert (J.C.S., 53, 679, 1888) obtained a compound, $C_{10}H_{14}Cl_8$. With bromine under the same conditions the product was $C_{10}H_{16}Br_4$, in which no substitution had occurred. Ostromisslenski (J. Russ. Phys. Chem. Soc., 48, 1132, 1916) obtained a chloride $(C_5H_8Cl_2)_x$ by careful working: in this, addition only had taken place. Gutta-percha and balata act similarly with chlorine, Caspari (J.S.C.I., 21, 1274, 1902) obtaining a product, $C_{20}H_{36}Cl_4$, and with bromine Ramsay, Chick and Collingridge (J.S.C.I., 21, 1367, 1902) obtained a product, $C_{10}H_{16}Br_4$, from gutta-percha. The bromination of caoutchouc, gutta-percha and balata in ice-cold chloroform solution is found to be practically independent of the time or the amount of bromine used, the bromide $(C_5H_8Br_2)_x$ always being the final product (Hinrichsen, below). The products after addition of iodine are somewhat unstable and often contain oxygen as well as iodine, indicating oxidation as well as addition.

Weber (Ber., 33, 791, 1900) acted on caoutchouc bromide with phenol and obtained a product $[C_5H_8(OC_6H_5)_2]_x$. Fisher, Gray and McColm (J.A.C.S., 48, 1309, 1926) and

Geiger (Helv. C.A., 10, 530, 1927) have confirmed and extended this original observation with interesting results. These are discussed more fully later (p. 39).

The hydrohalides are found to give definite addition products $(C_5H_9Cl)_x$, $(C_5H_9Br)_x$, and $(C_5H_9I)_x$, the last being somewhat unstable and apt to lose hydriodic acid. Hinrichsen, Quensell and Kindscher (Ber., 46, 1283, 1913) verified the preparation and composition of the caoutchouc hydrohalides, and Caspari (J.S.C.I., 24, 1274, 1905) prepared the hydrohalides of gutta-percha and balata, and isolated them as white, leathery flakes. All these halogen derivatives are best prepared in chloroform solution and purified by precipitation with alcohol. They are all white, tough, amorphous substances, very similar to each other. On standing, the iodides, hydrobromides and hydriodides turn brown through decomposition. Harries (Ber., 46, 733, 1913) found that on heating caoutchouc hydrochloride with pyridine the chlorine was removed and a regenerated caoutchouc not identical with the original was obtained; also that on attempting to reduce the hydrochloride with zinc and hydrochloric acid the product was still unsaturated (p. 76). Staudinger and Widmer (Helv. C. A., 7, 843, 1924) have prepared ethyl and methyl derivatives of hydrocaoutchouc by the action of zinc dialkyls on caoutchouc hydrochloride or hydrobromide, thus



The reaction is analogous for gutta-percha and balata: these products resemble hydrocaoutchouc very closely.

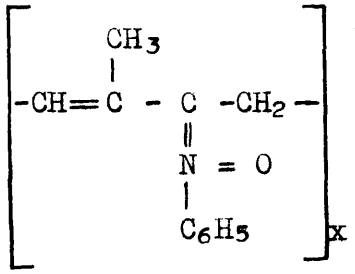
Oxides of Nitrogen.

Acting on caoutchouc with nitrogen trioxide, Harries (Untersuchungen, p.26) found a yellow powder $(C_{10}H_{15}N_3O_7)_2$ as chief product decomposing at 158 - 162°C: this he called "nitrosite C". The product from the action of the tetroxide is said by Harries to be very similar to nitrosite C. Emden (Ber., 58, 2522, 1925) however thinks it is a nitrosate of composition $C_{10}H_{16}N_2O_6$.

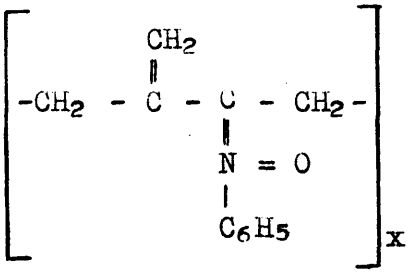
By the action of nitrogen tetroxide on gutta-percha Caspari obtained a buff coloured powder of composition $C_{10}H_{16}N_2O_4$. Prolonged treatment of this converted it with evolution of heat and gas into a yellow powder, $C_{10}H_{15}N_3O_7$, which he considered to be identical with Harries' nitrosite C. Treatment with nitric acid yields a yellow amorphous substance of composition $C_{15}H_{21}N_4O_{11}$, but with nitric oxide the action is accompanied by oxidation. Balata yields similar products; with nitrogen peroxide it gives $C_{10}H_{15}N_3O_7$ corresponding to the nitrosite C. Nitric oxide gives a yellow amorphous body, $C_{10}H_{16}NO_2$, in the formation of which oxidation

as well as addition seems to have taken place. Nitric acid yields a compound, $C_{15}H_{21}N_4O_{11}$, similar to the product from gutta-percha.

Bruni and Geiger (Rubber Age, 22, 187, 1927) have prepared iso-gutta-percha nitrone by the action of nitrosobenzene on the hydrocarbon, and this is found to be very similar to iso-caoutchouc nitrone obtained by the same method. The compound is given either of two formulae



or



These results have been confirmed by Pummerer, Andriessen and Gündel (Ber., 61, 1583, 1928) and by Staudinger and Joseph (Ber., 63, 2888, 1930).

Oxidation.

Both gutta-percha and balata are oxidised by exposure to air and light, gutta-percha somewhat more readily than balata. This applies to both purified and unpurified substances, but the action is very much faster and drastic in the case of the purified hydrocarbons, being hindered considerably by the presence of so-called "anti-oxidants" present in the crude material. The hydrocarbons become brown in colour and are brittle to the touch; they also have an acrid

smell. The products of this oxidation are resinous substances, but are not the same as the naturally occurring resins referred to previously.

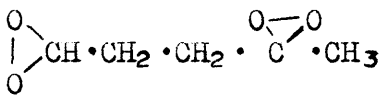
Ramsay, Chick and Collingridge (J.S.C.I., 21, 1367, 1902) oxidised an ethereal solution of gutta-percha with atmospheric oxygen and isolated a substance of nearly the same composition as alban, $C_{17}H_{26}O$. Oxidising in toluene solution, however, gave rise to a different product, a sticky solid, $C_{12}H_{14}O_4$, which decomposes on distillation under reduced pressure, giving a mixture of gaseous products and a yellow oil, $C_{12}H_{20}O_3$, of the odour of peppermint. Dawson and Porritt (Trans. Inst. Rubb. Ind., 2, 345, 1927) have oxidised balata with atmospheric oxygen. They exposed the purified hydrocarbon obtained from Venezuelan sheet to a current of air at ordinary temperature: the oxidation followed an autocatalytic course and yielded, as final product, a substance having the approximate composition $C_{10}H_{16}O_3$. During the progress of the reaction the presence of peroxides was indicated by the use of potassium iodide. A little formic acid was produced but no carbon dioxide was liberated and assuming that one carbon atom in every $(C_{10}H_{16})_n$ was converted into formic acid, they calculated that n = 112.

Recently Kemp, Bishop and Laselle (Ind. Eng. Chem., 23, 1444, 1931) have oxidised caoutchouc, gutta-percha and balata by exposing the purified hydrocarbons to oxygen at

room temperature for many weeks. This treatment resulted in the formation, in all three cases, of both volatile and amorphous solid products. The oxidation was so complex, however, that it was only possible to identify some of the oxidation products, in which they found a certain amount of similarity between the products from caoutchouc, gutta-percha and balata. The authors favour the hypothesis of a chain type of oxidation, and this is significant since Kirchof (Koll. Zeit., 13, 49, 1913) and Ostwald (J.S.C.I., 32, 179, 1913) have both suggested that air oxidation is a process of auto-oxidation brought about by means of unstable peroxides, and the presence of such peroxides has been observed. Mair and Todd (J.C.S.,386, 1932) have oxidised caoutchouc, gutta-percha and balata in chloroform solution with hydrogen peroxide under, as nearly as possible, identical conditions. They found as final product of a series of oxidation steps three compounds, one from each of the starting materials, all of the same approximate composition, $C_{50}H_{68}O_{28}$. These products are colourless, amorphous solids, saturated and alcoholic in character. Not enough data are available to state that these alcohols are identical, but a close similarity in structure is very probable. The results also indicate a similarity in molecular complexity between gutta-percha and balata hydrocarbons, while the caoutchouc hydrocarbon is considered as being of greater molecular complexity.

Harries (Ber., 18, 1195, 1905) found that on treatment of a chloroform solution of gutta-percha with ozone, an ozonide, $C_{10}H_{16}O_6$, was formed which gave on decomposition with steam a mixture of levulinic acid, aldehyde and levulinic aldehyde peroxide similar to the products from caoutchouc ozonide (p. 25), but in different proportions.

$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHO$ levulinic aldehyde

 levulinic aldehyde peroxide

$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH$ levulinic acid.

From this work Harries concluded that caoutchouc and gutta-percha were very similar, if not identical.

Much more work has been done on the oxidation of caoutchouc than on either gutta-percha or balata, but apart from a few cases of definite results, it is exceedingly difficult to draw any deductions since the products obtained have been in most cases very complex mixtures. For example, Robertson and Mair (J.S.C.I., 46, 41.T., 1927), using both acid and alkaline potassium permanganate as oxidising agents, have recognised as oxidation products of caoutchouc, formic, acetic, oxalic and levulinic acids, along with complex colloidal resin acids, and among the neutral products compounds of approximate composition $C_{35}H_{56}O_4$, $C_{30}H_{50}O_5$, $C_{26}H_{42}O_6$, $C_{24}H_{38}O_6$, $C_{20}H_{35}O_5$, $C_{30}H_{48}O_{10}$ etc., showing an

oxygen absorption proportional to the concentration of the oxidising agent. Peachey and Leon (J.S.C.I., 37, 55. T., 1918) showed that two molecules of oxygen for every $C_{10}H_{16}$ group are absorbed by thin films of carefully purified caoutchouc. Pummerer and Burkard (Ber., 55, 3458, 1922) found that a very dilute solution of very pure caoutchouc absorbs oxygen in agreement with the formula $(C_5H_8O)_x$, and also that perbenzoic acid reacts normally with caoutchouc to give an oxide $(C_5H_8O)_x$. These results are of intrinsic value in substantiating C_5H_8 as the fundamental group in caoutchouc and the allied substances, gutta-percha and balata.

Hydrogenation.

Since the chemical properties of caoutchouc, gutta-percha and balata depend, as stated previously, on the fact that they are unsaturated, the extent of which unsaturation is accepted as being one double bond per C_5H_8 group, perhaps like this,

$$\left[- CH_2 - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 - \right]$$

it would be thought that the hydrogenation of such a substance would be comparatively easy. This, however, has not been the case and the failure of early investigators to hydrogenate caoutchouc was one fact which hindered, for a long time, the

acceptance of the C_5H_8 group as being the basic unit of the caoutchouc molecule. Recently, however, this hydrogenation has been accomplished under both mild and drastic conditions, both methods giving definite products and both giving evidence in support of the C_5H_8 grouping. Indeed, the accomplishment of this reduction is now considered as one of the chief arguments in favour of this grouping and the reaction is considered to be represented thus

$$(C_5H_8)_x + XH_2 \longrightarrow (C_5H_{10})_x$$

Gutta-percha and balata have been similarly hydrogenated herein, and give the same evidence. It is readily seen how significant this evidence is in support of one double bond per C_5H_8 group.

A full discussion of this matter appears in the discussion preceding the account of the experimental work on hydrogenation (p. 59) and so nothing further need be said here, the above being sufficient to allow us to proceed to a discussion of constitution.

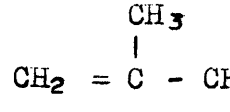
Constitution of Caoutchouc, Gutta-percha and Balata.

The first stage in the elucidation of the structure of caoutchouc is consideration of the polymerisation of the hydrocarbon isoprene to a caoutchouc-like substance.

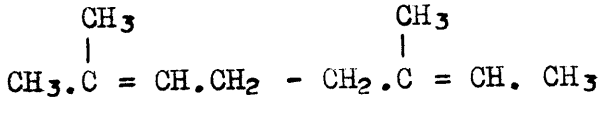
It has long been known that isoprene polymerises to a caoutchouc-like substance on treatment in various ways, Probably the first to observe this was Williams (Proc. Roy. Soc., 10, 516, 1860) who obtained his isoprene from the destructive distillation of caoutchouc. He stated that it "ozonised" and became viscous on standing. Other investigators also obtained this phenomenon by various methods, but Tilden (Chem. News, 65, 265, 1892) first observed that isoprene in sealed tubes polymerised and could be vulcanised like natural rubber. The isoprene he used was obtained by the pyrogenetic decomposition of turpentine. Weber (J.S. C.I., 13, 11, 1894) and Pickles (J.C.S., 97, 1685, 1910) have since confirmed this autopolymerisation, the latter by obtaining bromine and nitrogen trioxide derivatives from it and noting that they were very similar to those obtained from natural caoutchouc. It was discovered that other unsaturated substances could be polymerised to caoutchouc-like products: for example, Willstätter (Ber., 38, 1975, 1905) polymerised cyclo-octadiene, while other investigators obtained products from such substances as piperylene, dimethylisopropenyl carbinol, etc. These products were not identical with natural caoutchouc but they had the possibility of industrial use. At this time the methods of polymerisation were unsatisfactory since the most effective chemical agent,

hydrochloric acid, did not give pure products, and auto-polymerisation did not give satisfactory yields. Matthews (J.S.C.I., 31, 619, 1912) and Harries (Ann., 383, 157, 1911) simultaneously discovered that metallic sodium could polymerise isoprene comparatively rapidly. Although this sodium-caoutchouc had the advantage of speed in preparation, the best product is believed to be obtained by heating isoprene at 60°C in a closed vessel for a long time, Norris (Ind. Eng. Chem., 11, 819, 1919).

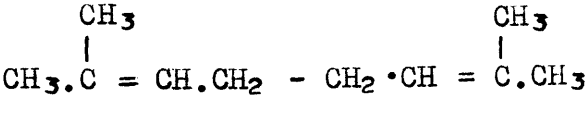
An interesting piece of work which provides evidence for the polymerisation of isoprene by metals has recently been published by Midgley and Henne (J.A.C.S., 51, 1215, 1929). By the action of metallic potassium on isoprene in presence of alcohol they have obtained a mixture of 2,6-, 2,7-, and 3,6-dimethyl-2,6-octadienes, the three possible dihydro dimers of isoprene.



isoprene



2,6-dimethyl-2,6-octadiene



2,7-dimethyl-2,6-octadiene

$$CH_3.CH = \overset{CH_3}{\underset{|}{C}}.CH_2 - CH_2.\overset{CH_3}{\underset{|}{C}} = CH.CH_3$$

3,6-dimethyl-2,6-octadiene.

No trace of cyclic compounds was found, thus it would appear that synthetic caoutchouc consists of a long chain or large ring of isoprene units joined through the 1,4 carbon atoms. The difference between synthetic and natural caoutchouc might be explained by a difference in the position of the methyl groups.

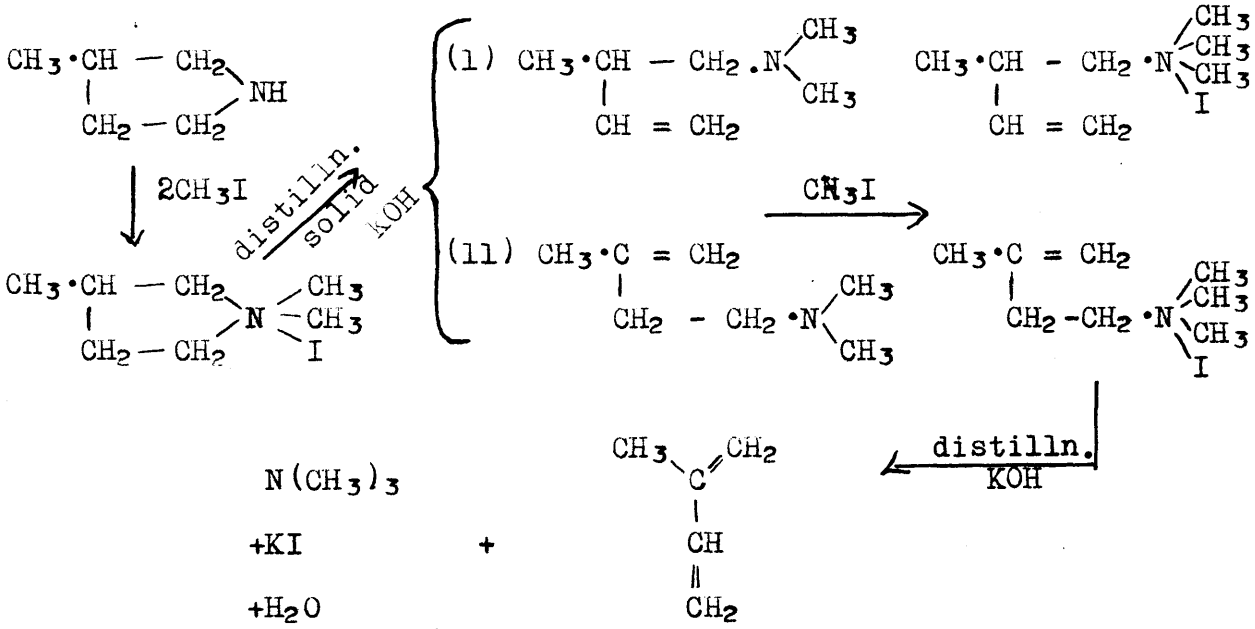
Harries (Ann., 383, 157, 1911) examined the ozonides of heat synthetic caoutchouc and sodium caoutchouc, and compared them with the ozonides of natural caoutchouc. He concluded that the heat synthetic caoutchouc was identical with natural caoutchouc, while the sodium polymerised product was probably different in structure. These he called "normal" and "abnormal" caoutchoucs. Now it is recognised that isoprene polymerises to products resembling caoutchouc, the next stage in the constitution of caoutchouc, etc., is to determine the constitution of isoprene.

The empirical formula is C_5H_8 and Tilden (Chem. News, 46, 129, 1882) suggested the structure

$$CH_2 = C(CH_3)\cdot CH = CH_2$$

The correctness of this guess was shown by the synthesis of

W. Euler (Ber., 30, 1989, 1897) who produced it from β-methyl pyrollidine by exhaustive methylation. The methiodide was first formed, then hydriodic acid eliminated to give a base. This in turn was converted into a methiodide, and this on removal of hydriodic acid yielded isoprene, thus



Isoprene.

If isoprene polymerises to caoutchouc and natural caoutchouc is a polymer of isoprene, then on distillation of caoutchouc, isoprene should be obtained, and this is found to be the case.

Dry distillation has been carried out by several investigators including Williams (Proc. Roy. Soc., 10, 516, 1860) and always a small quantity of isoprene has been obtained in the distillate. Recently Staudinger and Fritschi (Helv. C. A., 5, 785, 1922) have worked with purified caoutchouc and a vacuum

of 0·1 mms. pressure. The residue amounted to 36·50°/₀ and was one half as saturated as the hydrocarbon itself and was therefore a poly-cyclo caoutchouc. The distillate was carefully fractionated and resulted in 3·1°/₀ isoprene, 8·9°/₀ dipentene and small quantities of other hydrocarbons. The results are interpreted on the basis of a chain formula, the chain being supposed to break up and union taking place in groups of 2, 3, 4, etc. carbon atoms. Staudinger and Geiger (Helv. C. A., 2, 549, 1926) later worked with rapid distillation at ordinary pressures in an atmosphere of carbon dioxide; in this case the residue in the flask was much smaller. In one instance the isoprene fraction was 4·3°/₀ and in another 9°/₀, the corresponding dipentene fractions being 23·8°/₀ and 42°/₀. They found that the slower the distillation the greater the residue left undistilled.

The question arises why more isoprene is not obtained in the dry distillation of caoutchouc and also whether dipentene and the polyterpenes obtained are primary or secondary products. Under the conditions necessary for the distillation, isoprene polymerises easily to dipentene and other products and not to a caoutchouc-like substance, and furthermore, distillation of hydrocaoutchouc gives no isoprene but gives methyl-ethyl ethylene

$$CH_3 \cdot CH_2 \cdot \overset{CH_3}{\overset{|}{C}} = CH_2$$

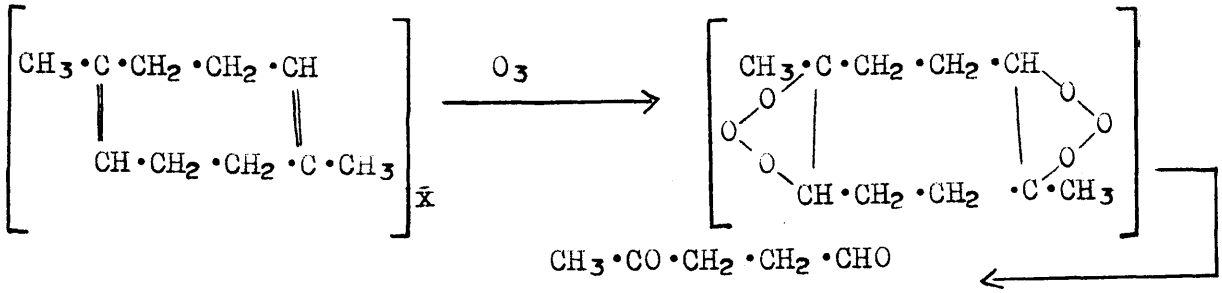
and in greater quantity than it gives its dimer $C_{10}H_{20}$,

Staudinger (Ber., 57, 1204, 1924). Thus it is possible that isoprene and its straight chain homologues are first obtained and these then polymerise into the polyterpene products obtained.

The work of Midgley and Henne (J.A.C.S., 51, 1215, 1929) has added more evidence in this field. They used large quantities of caoutchouc and isolated products which would usually escape notice, the yields of isoprene being large, 10°/o, and 20°/o for dipentene. Addition of magnesium to the mass increased the yield of the other products in the distillate from 0·86°/o to 9·05°/o. No fully saturated products were detected. By postulating that the single bond furthest removed from the double bonds is the most easily broken by pyrolysis, the authors are enabled to predict practically all of the compounds isolated.

It is now seen that the empirical formula of the caoutchouc hydrocarbon is C_5H_8, but how these groups are connected together, how many make up the actual molecule, and, in fact, whether the hydrocarbon consists of a single molecule or not, is not yet definitely known, but much work has been done in efforts to find out. The fundamental grouping has been shown to be C_5H_8, and not $C_{10}H_{16}$ as was formerly supposed. This has been substantiated in many ways as noted previously, and the measurements of the refractive index by Macallum and Whitby (Trans. Roy. Soc. Can., 18, 121, 1924) and of absorption spectra by Pummerer and Schiebe (Ber., 60, 2163, 1927) have definitely proved the existence of one double bond for each C_5H_8 group; not one-and-

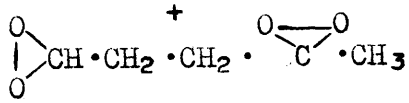
a-half per C_5H_8 as Gladstone and Hibbert (J.C.S., 53, 680, 1888) originally concluded. Since isoprene is the lowest product of the distillation of caoutchouc and has the same empirical formula as the caoutchouc hydrocarbon, and since it polymerises to a caoutchouc-like substance which is considered to be identical with natural caoutchouc, it is reasonable to suppose that caoutchouc itself is a polymer of isoprene. In the polymerisation, one of the double bonds is used up, leaving one double bond per C_5H_8 group. The main work on the elucidating of the resulting structure was carried out by Harries (Ber., 37, 2708, 1904 and Ber., 38, 1195, 1905): this was a study of the action of ozone on caoutchouc in solution. The resulting ozonide when purified analysed for $(C_5H_8O_3)$, showing the presence of one double bond per C_5H_8 group; molecular weight determinations indicated $C_{10}H_{16}O_6$. Hydrolysis of the ozonide gave levulinic aldehyde and levulinic aldehyde peroxide as chief products, and from this Harries formulated caoutchouc as a polymer of 1,5-dimethyl cyclo-octadiene, the formation of the above products being represented thus:-



$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHO$

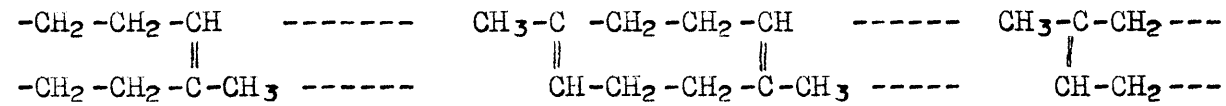
levulinic aldehyde

+

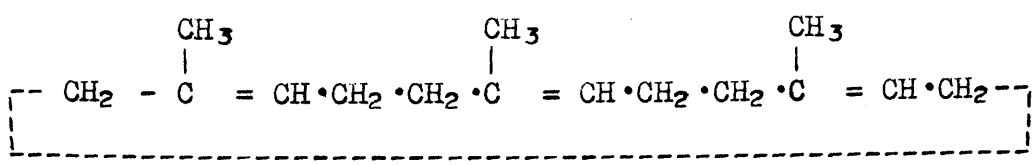


levulinic aldehyde peroxide.

Levulinic acid was also found, but was regarded as a secondary product obtained from the oxidation of the aldehyde by hydrogen peroxide liberated by decomposition of the aldehyde peroxide. According to Harries, the 1,5-dimethyl cyclo octadiene polymerises by saturation of partial valencies, the complex formed being easily depolymerised. This complex would be represented thus, the dotted lines indicating partial valencies:-

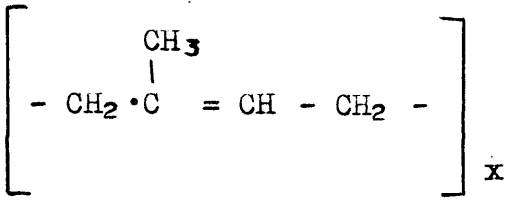


Pickles (J.C.S., 97, 1086, 1910) criticised this structure adversely. If ozone depolymerises the caoutchouc molecule then bromine should do likewise, but it is an experimental fact that it does not and the bromide $(C_5H_8Br_2)_x$ is a complex substance of much the same order of complexity as caoutchouc itself. If, otherwise, the polymerisation is chemical, i.e., by primary valencies, it must result in the elimination of double bonds and a reduction in unsaturation, but the bromide shows that this is not the case. Pickles formulated a mono-cyclic structure, the molecules of isoprene being chemically combined

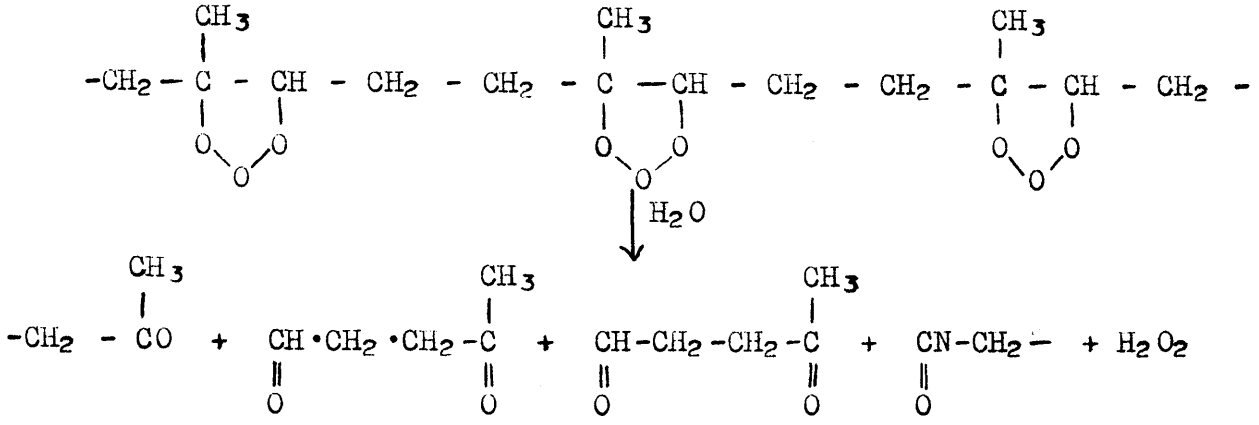


This structure allows one double bond per C_5H_8, the dotted line indicating an indeterminate number of isoprene groups. Since

this is the case, the structure is perhaps best represented thus:-



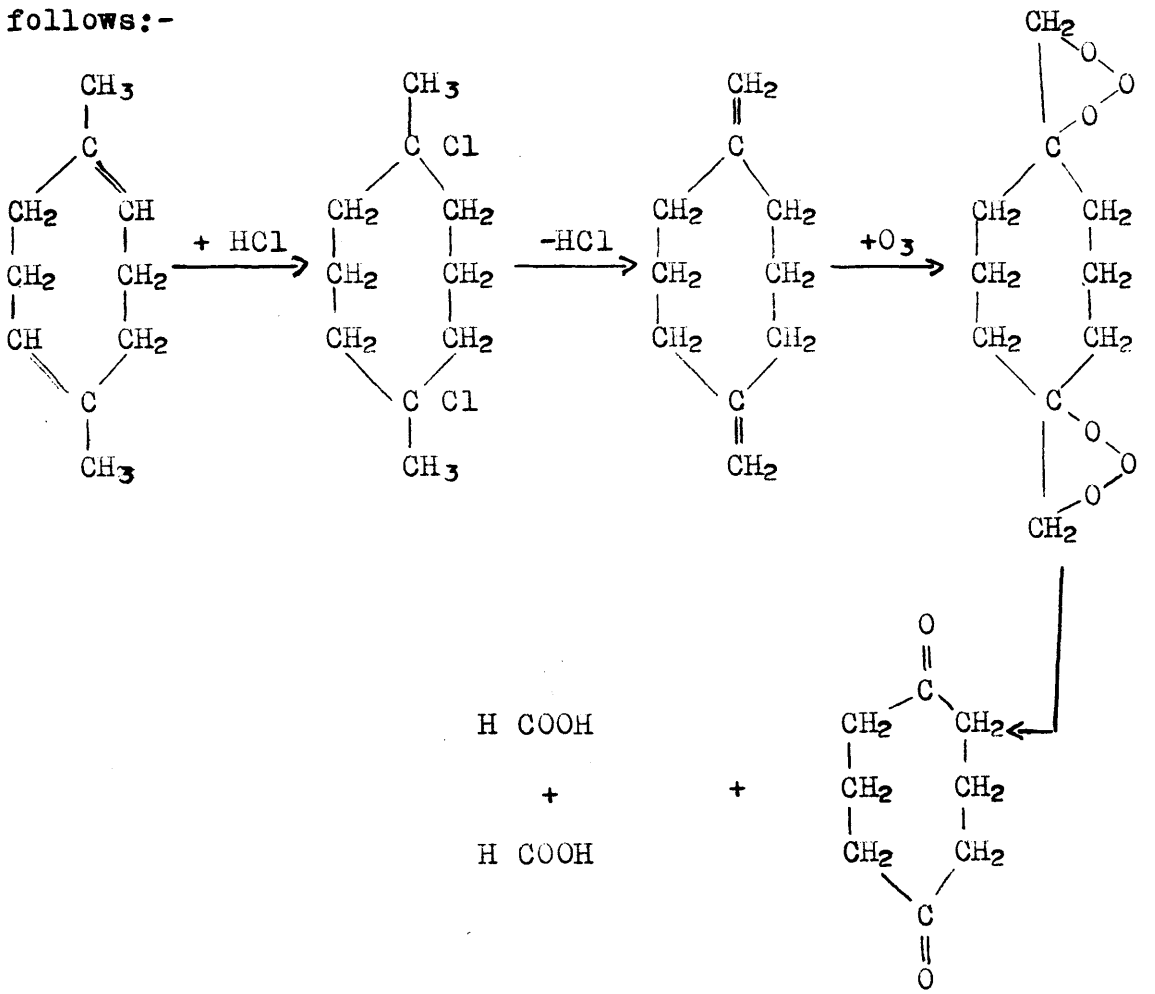
This structure also satisfies the ozonide decomposition, as follows:-



levulinic aldehyde.

Regenerated caoutchouc, obtained by heating the purified hydrochloride with pyridine in an autoclave and so removing the halogen acid, was studied by Harries (Ber., 46, 2590, 1913) by means of its ozonide. This gave some evidence of an 8-membered ring, and the products of hydrolysis of the ozonide were levulinic aldehyde and acid, 1,5-cyclo-octadione, formic acid and a keto acid $C_7H_{13}O$ COOH. To account for the production of such substances, it is assumed that the removal of the halogen acid may affect the distribution of the double bonds in different ways, the formation of the 1,5-cyclo-octadione being represented as

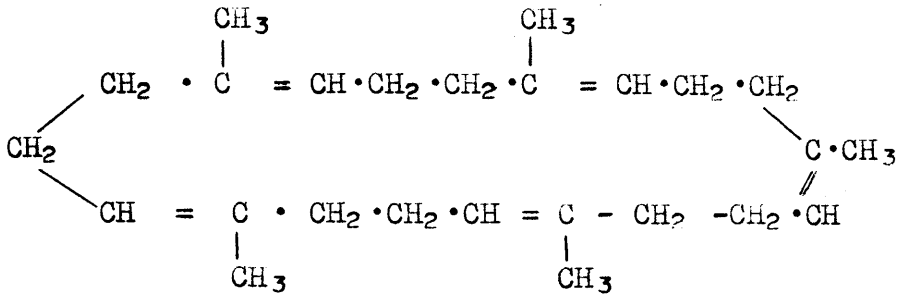
follows:-



In 1914 Harries (Ann., 406, 173, 1914), as a result of close examination of the decomposition products of the ozonide from regenerated or α-iso caoutchouc, abandoned his cyclo-octadiene formula. He found besides the usual levulinic aldehyde and acid, diacetyl propane $CH_3CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COCH_3$ and other polyketones and ketonic acids, and it was impossible to account for a triketone with eleven carbon atoms and a tetraketone with fifteen carbon atoms on the basis of an eight-carbon cycle.

Harries adopted the idea of a ring system, the ring containing

at least sixteen, probably twenty, carbon atoms, just like Pickles' model above,



and decided that the molecular weight which indicated $C_{10}H_{16}O_6$ as the formula of the ozonide was incorrect, and that the molecular weight of the ozonide was very much larger.

Ostromisslenski (J. Russ. Phys. Chem. Soc., 47, 1915 and 1932; 1915) showed by his work on cauprene bromide (polymerised vinyl bromide) $C_{32}H_{48}Br_6$, which is homologous with caoutchouc bromide, that it had a mono-cyclic structure, and so caoutchouc bromide also must possess a mono-cyclic structure $(-CH_2-CH_2\cdot C(Me)Br \cdot CH\ Br-)_x$, and since by the action of zinc dust and alcohol the bromide is converted readily and quantitatively into free caoutchouc, the latter must also possess a mono-cyclic structure ($-CH_2-CH_2-C(Me) = CH-$), the position of the methyl groups and double bonds to be fixed by the study of the ozonides. He further suggests a molecule $C_{40}H_{64}$ containing eight isoprene nucleii similar to the suggestion of Pickles.

Olivier (Rec. Trav. Chim., 40, 665, 1921) has repeated Harries' work on the ozonides and has come to the conclusion that no deductions as to the complexity of the caoutchouc molecule can

be drawn from the study of this substance. Boswell (I.R.J., 64, 983, 1922) has proposed a formula which contains no double bonds, and Kirchof (Koll. Chem. Beih., 16, 47, 1922) one in which the fundamental unit is $C_{10}H_{17}$. These formulae are now only curiosities since they were proposed before the hydrogenation had been accomplished and the C_5H_8 group with one double bond definitely established.

Harries (Ber., 38, 1195, 1905) formed an ozonide from gutta-percha similar to that from caoutchouc. The decomposition products were levulinic aldehyde and levulinic aldehyde peroxide similar to those from caoutchouc oxonide but in slightly different proportions. The chemical derivatives of gutta-percha are very similar to gutta-percha hydrocarbon in degree of complexity. This brings gutta-percha and caoutchouc into line as being structurally similar and, from what follows, balata must be considered so too. Recent work on the ozonides has substantiated Harries' work and ideas. Geiger (Gummi Ztg., 40, 2143, 1926) found that ozone gives a mixture of acids, one, a dicarboxylic acid, appears to have thirty carbon atoms in the molecule. Other oxidation work has shown the molecule to be not less than $(C_5H_8)_8$, Robertson and Mair, while Mair and Todd state that it is not less than $(C_5H_8)_{10}$. Pummerer, Ebermayer and Gerlach (Ber., 64, 809, 1931) have gone over the ozone oxidation very carefully with a view to isolating products derived from end groups. Harries concluded from his work that the molecule is built of pentadiene groups,

$= C(CH_3)-CH_2-CH_2-CH =$, or isopentene groups, $-CH_2-C(CH_3) = CH-CH_2-$, and that the double bonds are next to the methyl groups. Since he obtained nothing besides levulinic derivatives, he favoured the ring formula rather than the Weber open chain, since such an open chain should give other products besides levulinic derivatives; it should give products from the end groups of the chain thus,

$$\underset{a}{CH_3-C(CH_3)=} \quad \underset{b}{CH-CH_2-(CH_2-C(CH_3)=CH-CH_2)_n-CH_2-C(CH_3)=} \quad \underset{b}{CH-CH_3-CH=} \quad \underset{c}{C(CH_3)-CH=} \quad \underset{d}{CH_2}$$

This should give from (a) acetone, (b) levulinic aldehyde, (c) malonic aldehyde, (d) methyl glyoxal and formaldehyde, or

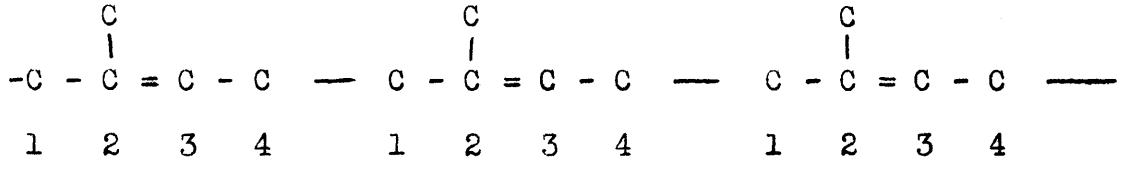
$$\underset{a}{CH_3-CH=} \quad \underset{b}{C(CH_3)-CH_2-(CH_2-CH=C(CH_3)-CH_2)_n-CH_2-CH=} \quad \underset{b}{C(CH_3)-CH_2-CH=} \quad \underset{c}{CH-C(CH_3)=} \quad \underset{d}{CH_2}$$

and from (a) acetaldehyde, (b) levulinic aldehyde, (c) aceto-acetic aldehyde, and (d) methyl glyoxal and formaldehyde.

Failure to find products from the end groups such as (a) and (d) led Harries to support a ring formula. Pummerer and his co-workers have worked very carefully, and although they have improved on Harries' results and obtained small quantities of substances possibly coming from end groups, acetic acid and pyruvic acid (oxidation product of methyl glyoxal, $CH_3CO \cdot CHO \longrightarrow CH_3 \cdot CO \cdot COOH$), the results are not affirmative enough to postulate definitely an open chain formation. Thus Pummerer leaves the question of ring

or open chain and the value of x open, and abandons his postulates (Ann., 438, 294, 1924; Ber., 60, 2167, 1927; Ber., 61, 1591, 1928) of a finite molecular weight and a definite ground molecule $(C_5H_8)_8$.

Midgley and Henne (J.A.C.S., 51, 1294, 1929) deduce from their work on polymerisation of isoprene to caoutchouc that synthetic caoutchouc, and probably natural caoutchouc, is a long chain or very large ring of isoprene units linked together by their 1 and 4 carbon atoms, e.g.,



Staudinger (Ber., 64, 1407, 1931) criticises Pummerer's work on ozone oxidation. Although it is possible to estimate the molecular weight of long chains by chemical methods when the compound has a characteristic end group, the method does not work with caoutchouc because the end groups amount to perhaps ·2% of the total molecule, thus no information can be got from the ozone oxidation as to the molecular size. Pummerer and Burkard (Ber., 55, 3458, 1922), from their hydrogenation work, concluded that there was present a ring system or an unusually long chain of isoprene nucleii, and this alternative seems to be about as far as these methods take us.

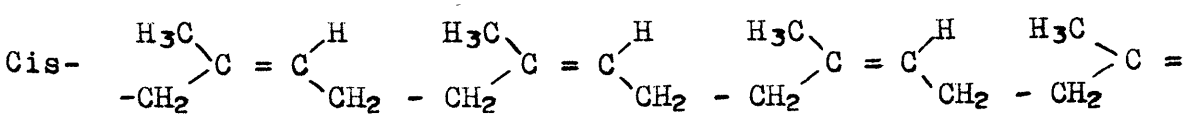
Staudinger postulates an extremely high molecular weight for caoutchouc, gutta-percha and balata hydrocarbons; also that

these are made up of many polymer homologues, and that the molecules are very long thread-like structures: he supports this view with a wealth of evidence (Ber., 61, 2575, 1928). Staudinger favours the idea of a mixture of hundreds of polymer homologues of which a separation is impossible since the boiling points are almost at the decomposition points, thus $(C_5H_8)_n$, n + 1, n + 2, etc., and the molecular weight of which mixture is very large, because hydrocaoutchouc on distillation yields a mixture of high molecular weight hydrocarbons, thus caoutchouc itself must have a high molecular weight. In a paper (Ann., 468, 1, 1929) Staudinger and Bondy bring gutta-percha into line with caoutchouc since the only difference observable between them is in their average molecular weights. "Gutta-percha is at all events more symmetrically built than caoutchouc, this is shown in the fact that it crystallises much more easily. Even in the unstretched state the molecules are in a lattice-like formation Clark (Ind. Eng. Chem., 18, 1131, 1926) and Hauser (K., 3,17 and 288, 1927). In the case of caoutchouc according to the experiments of J. R. Kratz the molecules are only arranged in a lattice after strong stretching. Thread-like molecules can arrange themselves in lattices easier than the large ring molecule of caoutchouc. It is possible to consider still other factors. It is possible with double bonds to have a cis., trans., formation. In gutta-percha we can have the cis-modification, and in caoutchouc the

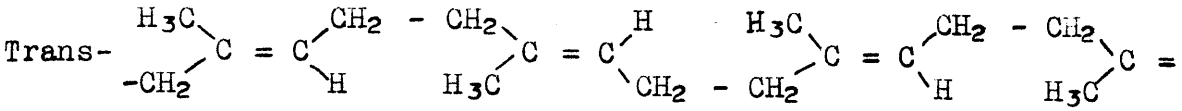
trans. Thus is cleared up the failure to convert caoutchouc into gutta-percha, since now we see caoutchouc and gutta-percha and their degradation products form two different polymer-homologous series, which hitherto had unknown differences in structure. Only by cyclisation does such a deep acting alteration occur in the molecule that the products from caoutchouc and gutta-percha are identical." (p.29).

Further, Staudinger (Ber., 63, 927, 1930), from his long experience of caoutchouc and other highly polymerised products, and his recent work on balata and gutta-percha (Ann., 468, 1, 1929: Ber., 63, pp. 724, 730, 734, 1930) concludes that to all intents and purposes gutta-percha and balata are identical and different from caoutchouc which, for one thing, shows no tendency to crystallise, while gutta-percha and balata do. The difference between gutta-percha and balata, and caoutchouc extends to their hemi-colloid degradation products. As was shown, two series of polymer-homologous polyprenes exist; on the one side is caoutchouc and its degradation products, and on the other gutta-percha and balata and their degradation products. The difference is attributed to a cis, trans, formation, thus:-

Gutta-percha and Balata

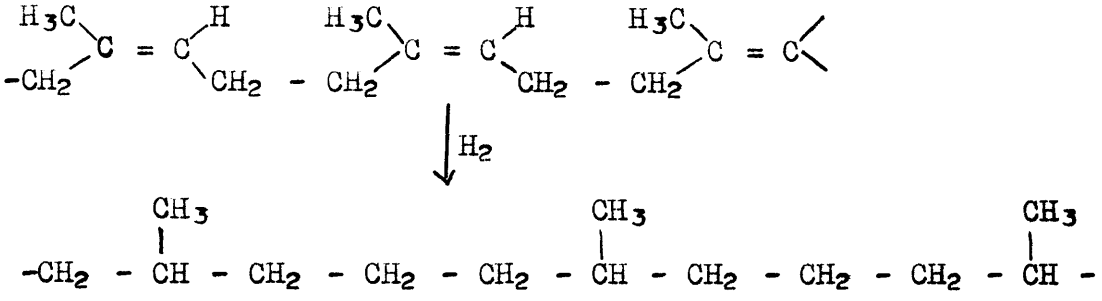


Caoutchouc

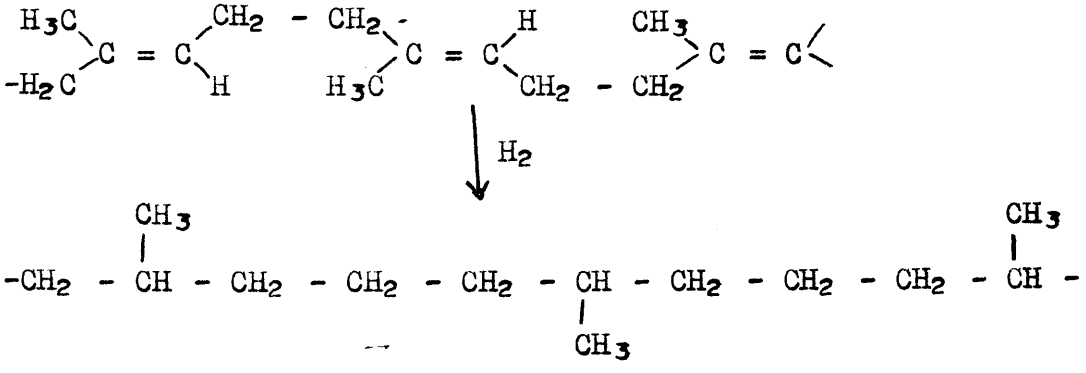


To this may be added the fact that on reduction of the double bonds the essential structural differences disappear, and so, for example, hydro-caoutchouc, hydro-gutta-percha and hydro-balata all have the same appearance.

Gutta-percha and Balata



Caoutchouc



Further, the density of crystalline balata is 0·9571, while that of amorphous caoutchouc is 0·9238. This cis- form is more tightly packed than the unsymmetrical trans- form. The best

argument for this hypothesis is that both gutta-percha and balata crystallise in the unstretched condition and therefore it seems probable that their molecules have a symmetrical structure, while caoutchouc only shows crystalline when strongly stretched. Staudinger further postulates that the molecules of gutta-percha and balata are stiff thread-like structures and that the molecules of caoutchouc approximate to this structure. Sheppard, Nietz and Keenan's (Ind. Eng. Chem., 21, 126, 1929) results support this postulate of a flat molecule. They found that when a solution of caoutchouc in petroleum ether is allowed to form a film on mercury insufficient to cover the entire surface, its thickness is only 1·5Å. This is very small since for example, a molecular film of stearic acid is 21 Å thick.

Of the molecular size of these hydrocarbons much has been written, principally from two sides, the one supporting a definite basic molecule, e.g., $(C_5H_8)_8$, the other supporting an extremely large molecule, e.g., $(C_5H_8)_{1000}$.

Pummerer (Ber., 55, 2458, 1922; Ann., 438, 294, 1924; Ber., 60, 2163, 1927; Ber., 60, 2167, 1927; Ber., 61, 1591, 1928; Ber., 62, 2628, 1929) and his co-workers advanced evidence from hydrogenation, X-ray spectra, cryoscopic molecular weight estimations, and the molecular weight of the nitrone, for the molecular weight of caoutchouc. He came to the conclusion that the ground molecule was $(C_5H_8)_8$ and advanced arguments from the above in favour of this. Since then, however (Ber., 64, 809, 1931), he seems to have abandoned this idea and is leaving the question

open. Staudinger, on the other hand, has always criticised Pummerer's hypothesis and he postulates an enormous molecular weight for caoutchouc and for gutta-percha and balata. From the relation between viscosity and molecular weight Staudinger and his co-workers have worked out the molecular weights of these substances (Ber., 63, pp.724, 730, 734, 921; 1930; Helv. C. A., 13, pp.1321, 1324, 1334, 1350, 1355, 1361, 1368, 1375; 1930; Ann., 488, 127, 1931), taking all derivatives and exceptions into account, and they consider that all three hydrocarbons are "eucolloids" and consist of macromolecules, the average molecular weights being in the region of:-

Caoutchouc .. 68,000

Gutta-percha.. 50,000

Balata .. 50,000

and made up of hundreds of polymer homologues. A good argument for the high molecular weights is the colloid nature and high molecular weights of their reduction products and derivatives, e.g., bromides; so also is the fact that a compound ($C_{50}H_{100}$) is found in the distillation products of hydrocaoutchouc.

Recently (Helv. C. A., 15, 221, 1932) Staudinger and Leupold have advanced a further fact in support of their hypothesis. Taking a series of hydrocarbons with numerous methyl side chains including octomethyldotriacontane $C_{40}H_{82}$, hexahydrosqualine $C_{30}H_{62}$, and tetra-methyl-hexadecane $C_{20}H_{42}$, and others,

from the lowest member isopentane C_5H_{12} to the highest, hydrobalata $(C_5H_{10})_{700}$, they show the gradual gradation in properties up the series showing the validity of the high molecular weight hypothesis. Also comparing with hydrocarbons with normal chains the great differences in solubility are remarkable. Those paraffins with many methyl side chains are remarkable for their solubility in ether, benzene, chloroform, and the very highest members are easily soluble in those solvents. Great solubility differences only show in alcohol and acetone, in which the highest members are insoluble. On the other hand, paraffins with normal chains show a remarkable falling off of solubility in all solvents with increase in molecular weight and at the 100 carbon atoms stage the substances are insoluble in all solvents. The easy solubility of hydrocaoutchouc is therefore a property which all high molecular weight paraffins with methyl side chains have in common.

The question of structure and molecular size of caoutchouc, gutta-percha and balata is not yet settled, but the present day picture of them is that they are mixtures of unseparable polymer homologues, such polymers consisting of very long chain molecules made up of isoprene nucleii joined at the 1 and 4 carbon atoms, each group of C_5H_8 having one double bond. Gutta-percha and balata are considered to be practically identical, and different from caoutchouc in some way. Whether it is a case of cis- and trans- formation, is not yet certain, but this is a possibility.

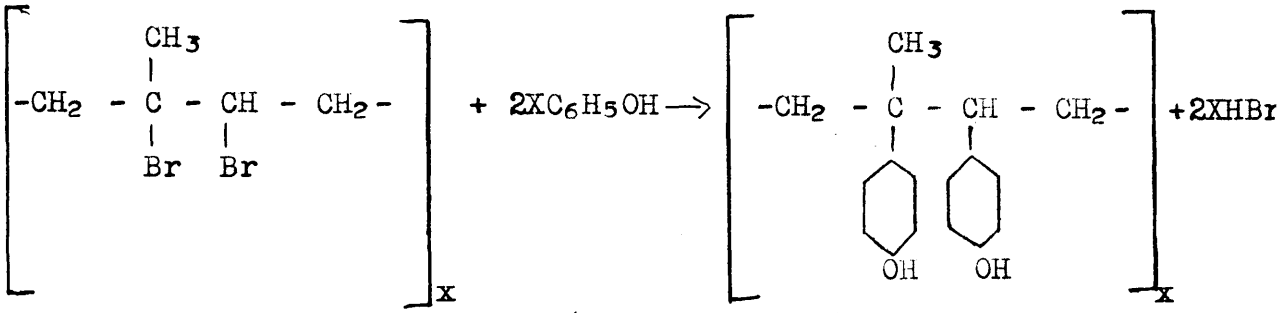
E X P E R I M E N T A L.

A.

Condensation of Balata Bromide with Phenols and Phenolic Ethers.

The Friedel and Craft reaction was first applied to caoutchouc bromide by C. O. Weber (Ber., 33, 791, 1900) who found that phenol reacted with caoutchouc bromide in presence of aluminium chloride at 80 - 150°C with evolution of hydrobromic acid, and from this, a compound which he represented as $[C_{10}H_{16}(OC_6H_5)_4]_x$, could be isolated. This substance he named "tetroxyphenyl-polyprene". It was soluble in alcohol, acetone, ether and aqueous alkalies and insoluble in benzene, chloroform and petroleum ether. Since, however, he could get no similar reaction with anisole, Weber concluded that the hydroxyl group formed the point of attack and therefore formulated the compound as an ether. This investigation has since been repeated by Fisher, Gray and McColm (J.A.C.S., 48, 1309, 1926). They found that the product could be methylated easily and that this methylated product was soluble in benzene and insoluble in aqueous alkalies. This shows that the phenol condensation product contains free hydroxyl groups and that the linkage between the phenol and the caoutchouc carbon atom is at the ring. This linkage was assumed to be in the para position to the hydroxyl

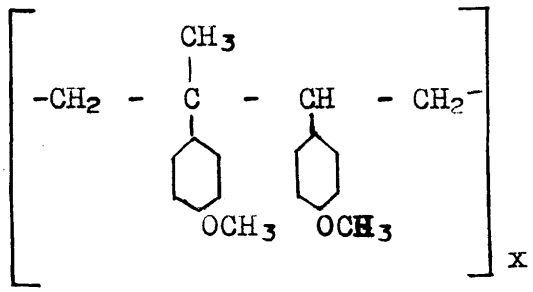
group and therefore the reaction was formulated thus



They named this substance di (hydroxyphenyl) hydrorubber, and the methylated product di (methoxyphenyl) hydrorubber. The yield was found to be practically quantitative if anhydrous ferric chloride was used instead of aluminium chloride. The compounds gave no depression of the freezing point of benzene and showed colloidal properties, so it is inferred that the parent hydrocarbon must have very large colloidal molecules.

In 1927 Geiger (Helv. C. A., 10, 530, 1927) extended this work to a series of phenols and phenolic ethers and also to gutta-percha bromide which he found reacted in an exactly similar manner to caoutchouc bromide. Details of results and reactions of caoutchouc bromide with phenol, o-, m- and p-cresol, resorcinol and pyrogallol, also with anisole, phenetole and α-naphthyl methyl ether are given. With phenolic ethers the reaction was slower than with phenols, and the yields were poor. It is remarkable that by condensing caoutchouc bromide with anisole Geiger obtained a compound in one step identical with that obtained by Fisher, Gray and McColm from methylation of the phenol condensation product, as is shown by their melting points: Geiger's product

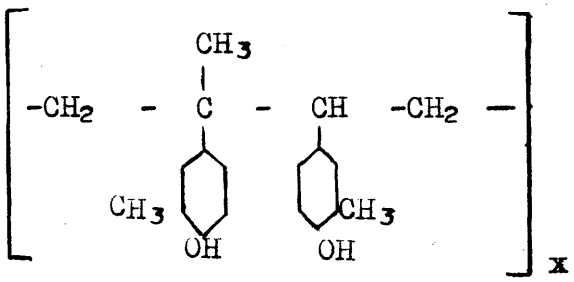
melting at 150 - 160°C., and Fisher, Gray and McColm's at 151 - 156°C (corr.). The substance is formulated



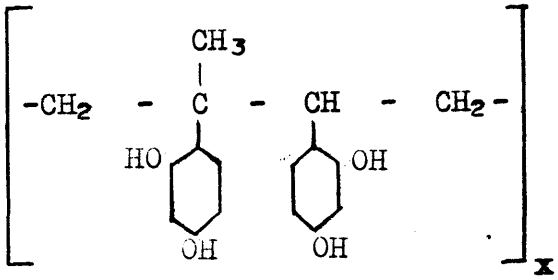
Dimethoxy-diphenyl-hydrocaoutchouc.

Geiger also prepared the benzoates of the phenolic products by the Schotten-Baumann reaction and so confirmed the presence of hydroxyl groups.

With gutta-percha bromide and phenol, o-, m- and p-cresol and resorcinol he obtained compounds similar in all ways to those obtained from caoutchouc bromide, except that their melting points were somewhat lower. Geiger also assumes a linking para to the hydroxyl group from analogy with simpler compounds, e.g., p-bromotoluene (Schöpff, Ber., 24, 3769, 1891), and formulates the compounds, e.g., with o-cresol and resorcinol as



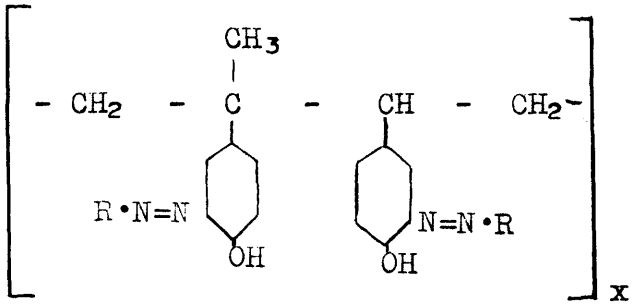
Dihydroxy-dimethyl-diphenyl-hydrocaoutchouc ;



Tetrahydroxy-diphenyl-hydrocaoutchouc.

No depression of the freezing point of benzene was observed with any of the compounds, and those examined with X-rays gave "amorphous" rings.

Geiger (ibid, p.539) has examined the products obtained by coupling some of these condensation products with diazotised aromatic amines. The products from the phenol and resorcinol compounds are easily soluble in alkalies and can be precipitated with acids: in dilute solution they act as indicators for acids and bases. The coupling is assumed to take place on the benzene ring adjacent to the hydroxyl groups, thus



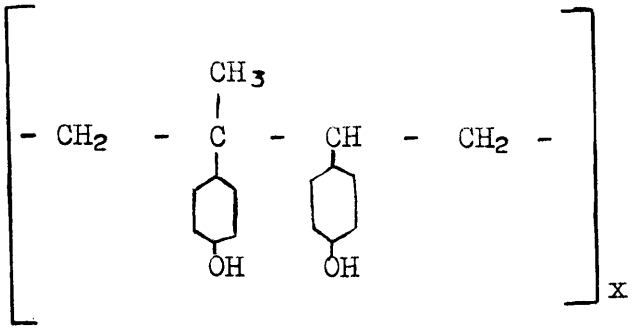
These products also have colloidal properties and are of very high molecular weight.

Staudinger (Kautschuk, p.63, 1926) indicates that unpublished work shows that products such as have been described are much more complicated than is supposed and their formation involves not only condensation but cyclisation. This has not been substantiated and in view of the results described above and later it is very probable that only condensation occurs.

The present work was undertaken with a view to extending these investigations to balata bromide and comparing the results from all three hydrocarbons. Newly prepared balata bromide was found to react very readily with excess phenol, o-, m- and p-cresol, resorcinol, and α-naphthol in presence of about 40°/

of its weight of anhydrous ferric chloride at a temperature of 100 - 120°C., with evolution of hydrobromic acid. The resulting compounds, purified by repeated solution and precipitation, are very soluble in alkalies and in pyridine solution with p-nitrobenzoyl chloride give p-nitro-benzoates very readily, thus showing the presence of free hydroxyl groups. A similar reaction was carried out at a slightly higher temperature with anisole and phenetole. The yields were low but could be easily isolated by their solubility in acetone and ethyl acetate. Since the corresponding anisole and phenetole condensation products with gutta-percha bromide have not been described, these were prepared in order to complete the series.

Analysis of the phenol condensation product agrees very closely with the formula $[C_5H_8(C_6H_4OH)_2]_x$ dihydroxy-diphenyl-hydrobalata, and the other products give analyses which agree with similar formulae. Fisher, Gray and McColm and Geiger (above) assumed that the phenyl group was attached to the hydrocarbon nucleus in the para position to the hydroxyl group. This has been proved by oxidation of dihydroxy-diphenyl-hydrobalata in acetone solution with potassium permanganate. From this, p-hydroxy-benzoic acid was isolated and confirmed by means of its acetyl derivative prepared by the method of Chattaway (J.C.S., 2495, 1931). Thus the above assumptions are correct and the compound is to be formulated p-dihydroxy-diphenyl-hydrobalata



These compounds are coloured amorphous powders whose melting points are not sharp but usually extend over a few degrees. They are mostly soluble in acetone, ethyl acetate and pyridine, and insoluble in petroleum ether, acids and water. In addition the phenolic products are soluble in alkalies and very slightly soluble in benzene, while the phenolic ether products are soluble in benzene and insoluble in alkalies. None of the compounds give any depression of the freezing point of benzene and molecular weights by the Rast method give variable results; while, according to Staudinger (Ber., 61, 2575, 1928), this method does not give reliable results for this type of compound. From the colloidal nature of the solutions it is deduced that the molecules, even in the nitrobenzoates, three reaction stages from the hydrocarbon, are not far removed in size from those of the latter. Many of the compounds give fluorescent solutions in certain solvents and the resorcinol condensation products of both gutta-percha and balata were found to be good indicators for acids and bases and also, which is unusual, for silver salt solutions, being adsorbed on to the silver halide precipitate at the equivalence point.

The products from caoutchouc, gutta-percha and balata are similar in that they are all coloured, amorphous substances of high molecular weight giving colloidal solutions, thus upholding Staudinger's postulate that the very large colloidal caoutchouc, gutta-percha and balata molecules are held together by normal valency and not by association. No reference has been made to indicator properties in tetrahydroxy-diphenyl-hydrocaoutchouc, while tetrahydroxy-diphenyl-hydrogutta-percha and -hydrobalata are identical in this respect. The melting points of the balata and gutta-percha compounds are similar and somewhat lower than those of the corresponding caoutchouc compounds. From the results no very definite resemblances or differences can be deduced and strongly held because of the difficulty in correlating different workers' results, and the difficulty of purifying these substances.

The balata was purified by the method described on p. 3, and from this balata bromide was prepared as described by Weber in "The Chemistry of India Rubber" (London), p.32. A 5°/o solution of bromine in chloroform was added carefully from a burette to an ice-cooled 1°/o solution of balata in chloroform until the colour was no longer discharged, a slight excess then being added. This solution was then run in a thin stream into a large volume of ice-cooled absolute alcohol and a beautiful white powdery precipitate was thrown down. This was filtered,

washed with alcohol and dried at about 30°C. The yield of bromide was 90°/₀.

p-dihydroxy-diphenyl-hydrobalata.

6·25 gms. balata bromide and 2·5 gms. ferric chloride were added to 20 gms. of melted phenol in an R.B. flask and the mass heated on an oil-bath at 100 - 120°C. for $2\frac{1}{2}$ hours. Hydrobromic acid was evolved quite vigorously and after the above time all the balata bromide had dissolved, leaving a thick brown liquid in the flask. This, after cooling, was diluted with 50 ccs. alcohol and the solution then poured into 500 ccs. warm dilute hydrochloric acid, giving a dark brown precipitate. This was filtered, dissolved in acetone and reprecipitated with dilute acid. The purification was repeated once or twice and the final product was 5 gms. of a chocolate brown powder which shrinks at 130°C., M.P. 195 - 200°C. This substance is soluble in alkalies, alcohol, ethyl acetate and acetone, giving dark coloured solutions. It is only slightly soluble in ether and benzene, and is insoluble in acids, water and petroleum ether. The ethyl acetate and benzene solutions are faintly fluorescent.

·1500 gms. subst. gave ·1000 gms. H_2O and ·4390 gms. CO_2.

·0910 gms. " " ·0585 gms. " " ·2673 gms. "

°/₀ Carbon found 79·8°/₀ 80·1°/₀: calculated 80·3°/₀

°/₀ Hydrogen " 7·40°/₀ 7·15°/₀: " 7·09°/₀

$$[C_5H_8(C_6H_4OH)_2]_x$$

The product gave no depression of the F.Pt. of benzene. Molecular weight estimations by the Rast method in camphor gave the following results:-

Concentration	1 : 5	depression	5·25°	mol. weight	1530
"	1 : 10	"	4·1°	" "	1020
"	1 : 40	"	1·3°	" "	767

Acetate. ·45 gms. p-dihydroxy-diphenyl-hydrobalata heated for half an hour with 4 ccs. redistilled acetic anhydride, poured into water, filtered, washed with sodium carbonate and then water, gave ·4 gms. of a yellow brown powder, M.Pt. 218 - 220°C. The acetate is soluble in acetone, ethyl acetate, pyridine, and benzene, and insoluble in alkalies, acids, water, ether and petroleum ether.

·1010 gms. subst. gave ·0600 gms. H_2O and ·2785 gms. CO_2

·0850 gms. " " ·0501 gms. " " ·2331 gms. "

°/₀ Carbon	found	75·2°/₀	74·8°/₀	Calculated	74·6°/₀
°/₀ Hydrogen	"	6·60°/₀	6·55°/₀	"	6·51°/₀

$$[C_5H_8(C_6H_4 \cdot O \cdot OC \cdot CH_3)_2]_x$$

Dinitrobenzoate. 1 gm. p-dinydroxy-diphenyl-hydrobalata in 30 ccs. pyridine mixed with 4 gms. p-nitrobenzoyl chloride in 30 ccs. pyridine and allowed to stand for 24 hours. The solution was then poured into ice-cold dilute sulphuric acid, the precipitate filtered, washed with sodium carbonate and then with water, dried, gave 1·5 gms. of a brown coloured compound, M.Pt. 87 - 90°C.

The dinitrobenzoate is soluble in alcohol, pyridine and acetone, and is insoluble in alkalies, acids, water and petroleum ether.

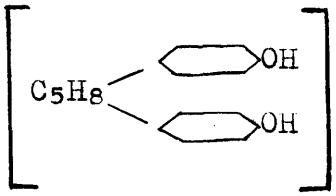
Nitrogen by Dumas' method: found 5·21°/° 5·13°/°

calc. 5·073°/°

$[C_5H_8(C_6H_4 \cdot O \cdot OC \cdot C_6H_4NO_2)_2]_x$.

Oxidation of p-dihydroxy-diphenyl-hydrobalata.

20 gms. of p-dihydroxy-diphenyl-hydrobalata prepared as before were oxidised in purified acetone solution with the theoretical quantity of finely ground potassium permanganate, 80 gms. The permanganate was dusted into the solution in small quantities with constant stirring at room temperature.



$\xrightarrow{13\ O}$ $2C_6H_4 \cdot OH \cdot COOH + 3H_2O + 3CO_2$

The solution was then evaporated to dryness, leached with hot water and a stream of sulphur dioxide passed until all the manganese dioxide had disappeared. The resulting yellowish white flocculent precipitate was filtered and found to be partly soluble in hot water, the insoluble part consisting of complex resin acids. The aqueous solution was evaporated and a solid separated. This was recrystallised from water and found to be an acid, M.Pt. 211°C., without further purification. An acetyl derivative prepared by dissolving the acid in a little more than the theoretical amount of sodium hydroxide, cooling in ice, and adding acetic anhydride

rapidly, the product coming out in three minutes (Chattaway, J.C.S., 2495, 1931), had a M.Pt. 186°C. Thus the acid was p-hydroxybenzoic acid, and the linking in the phenol condensation product is proved to be para to the hydroxyl group.

Dihydroxy-dimethyl-diphenyl-hydrobalata.

2 gms. balata bromide, 1 gm. anhydrous ferric chloride and 10 gms. p-cresol were heated in an R. B. flask at 100 - 120°C on an oil bath for 2 hours. Hydrobromic acid was evolved leaving a dark brown coloured liquid which, when cool, was poured into 400 ccs. 1°/o sodium hydroxide and filtered. The residue was extracted at 80°C with 150 ccs. dilute hydrochloric acid to dissolve out the iron salts. This was again filtered and the residue dissolved in 75 ccs. acetone which, when poured into dilute hydrochloric acid, gave a greenish gray coloured precipitate. This when purified by solution and precipitation gave 1·5 gms. of di-hydroxy-dimethyl-diphenyl-hydrobalata, M.Pt. 167 - 169°C., soluble in alkalies, acetone, ethyl acetate, alcohol and pyridine, slightly soluble in ether and benzene, insoluble in acids, water and petroleum ether. In dilute solution a colour change is observable with change from acid to alkaline.

·1028 gms. subst. gave ·0722 gms. H_2O and ·3026 gms. CO_2

·0930 gms. " " ·0651 gms. " " ·2742 gms. "

°/o Carbon	found 80·28°/o	80·39°/o	Calculated from	80·8%
°/o Hydrogen	" 7·80°/o	7·78 °/o	$[C_5H_8(C_6H_3 \cdot OH \cdot CH_3)_2]_x$	7·80%

No depression of the F.Pt. of benzene was observed and molecular weights by the Rast method in camphor gave,

Concentration	1 : 5	depression	5·5°	Mol. weight	1470
"	1 : 10	"	4·65°	" "	862
"	1 : 40	"	1·75°	" "	581

Dinitrobenzoate. ·43 gms. dihydroxy-dimethyl-diphenyl-hydrobalata in pyridine solution mixed with 2·5 gms. p-nitrobenzoyl chloride in pyridine and allowed to stand for 24 hours yielded ·6 gms. of a light brown coloured powder, M.Pt. 143 - 145°C., soluble in ethyl acetate, acetone and alcohol, slightly soluble in ether and benzene, in soluble in alkalies, acids, water and petroleum ether.

Nitrogen (Dumas) found 4·94°/o 4·90°/o

$[C_5H_8(C_6H_3 \cdot CH_3 \cdot O \cdot CO \cdot C_6H_4 \cdot NO_2)_2]_x$ calc. 4·83°/o.

Similar compounds were obtained by condensing with m- and o-cresol. With m-cresol 2·1 gms. of a greenish gray substance shrinking at 140°C and M.Pt. 165 - 169°C were obtained. The dinitrobenzoate was a yellowish brown coloured compound M.Pt. 146 - 148°C. Again there was no depression of the F.Pt. of benzene and molecular weights in camphor gave the following:-

Concentration	1 : 5	depression	5·6°	Mol. weight	1430
"	1 : 10	"	4·6°	" "	840
"	1 : 40	"	1·7°	" "	568

With o-cresol 1·8 gms. of a brown coloured compound, M.Pt. 193 - 195°C., were obtained. The dinitrobenzoate was a brown

coloured product shrinking at 140 - 145°C., M.Pt. 190 - 192°C. Molecular weights in camphor gave,

Concentration	1 : 5	depression	5·26°	Mol. weight 1520
"	1 : 10	"	4·55°	" " 879
"	1 : 40	"	1·81°	" " 552

The solubilities of these compounds are exactly similar to those of the product from p-cresol and its nitrobenzoate derivative.

Tetrahydroxy-diphenyl-hydrobalata.

2·5 gms. balata bromide, 1·25 gms. ferric chloride, and 12 gms. resorcinol were heated together on an oil bath at 100 - 130°C. for $2\frac{1}{2}$ hours. Hydrobromic acid was vigorously evolved and finally a thick brown liquid remained. 150 ccs. alcohol were added and the mass digested at 80°C. for 1 hour. The liquid was then poured into 500 ccs. dilute hydrochloric acid and the product was precipitated, leaving a bright red coloured solution. The precipitate filtered and purified by resolution and reprecipitation yielded 2·9 gms. of a deep red coloured product, M.Pt. 220°C., soluble in alkalies, acetone, alcohol and ethyl acetate, slightly soluble in ether and benzene, insoluble in acids, water and petroleum ether.

·1000 gms. subst. gave ·0556 gms. H_2O and ·2610 gms. CO_2

·1100 gms. " " ·0634 gms. " " ·2860 gms. "

°/o Carbon	found 71·20°/o	70·90°/o	Calculated from	71·30°/o
°/o Hydrogen	" 6·18°/o	6·40°/o	$[C_5H_8(C_6H_3(OH)_2)_2]_x$	6·34°/o

No depression of F.Pt. of benzene. Molecular weights in camphor,

Concentration	1 : 5	depression	4·9°	Mol. weight	1280
"	1 : 10	"	4·4°	" "	853
"	1 : 40	"	3·5°	" "	286

Tetranitrobenzoate. 1·3 gms. of above compound in 30 ccs. pyridine mixed with 5 gms. p-nitrobenzoyl chloride in 30 ccs. pyridine and allowed to stand for 2 days yielded 1·5 gms. of a violet red coloured substance, M.Pt. 195 - 200°C.

Nitrogen (Dumas) found 6·33°/o 6·41°/o

Calculated from $[C_5H_8(C_6H_3(O\cdot CO\cdot C_6H_4\cdot NO_2)_2)_2]_x$ 6·35°/o

The alcohol solution of tetrahydroxy-diphenyl-hydrobalata showed very marked green fluorescence in alcohol solution, and further a dilute alcohol solution was found to be an excellent indicator for acid and base, the colour change being from red in alkali to straw yellow in acid. The P_H range of the change was found

(1) by comparing with a series of B. D. H. indicators,

(11) by using solutions of known P_H value from acetic acid and ammonia,

(111) by using B. D. H. Universal Buffer solution.

From (1) the approximate P_H range was found to be 5·2 - 6·8 using methyl orange, phenolphthalein, phenol red, bromo-cresol green, etc., etc.: from (11) the range was found to be more nearly 5 - 6 using standard molecular solutions of acetic acid

and ammonia, and finally from (111) the P_H range was 5·4 - 5·9 for the free substance in alcohol, and for the sodium salt in water, which gives a very clearly defined change, 5·67 - 5·9, the colours being the same in both cases, red in alkalies and yellow in acids.

This compound was also found to be a reliable indicator for silver salts, e.g., adding standard potassium chloride to standard silver nitrate solution with the indicator present, just at the equivalence point the colour is adsorbed from the solution on to the silver chloride precipitate. The sodium salt, got by shaking some tetrahydroxy-diphenyl-hydrobalata with insufficient sodium hydroxide to dissolve it, in aqueous solution gave better results. The colour is removed from the precipitate if a drop of silver nitrate solution is added. Using solutions of unknown strength the results with bromide and iodide were excellent, while those with chloride were not quite so exact.

Since Geiger (Helv. C. A., 10, 530, 1927) makes no mention of similar properties in tetrahydroxy-diphenyl-hydro-gutta-percha, this compound was prepared and gave 3 gms. of a dark orange coloured substance, M.Pt. 270°C. The alcohol solution of this product is extremely fluorescent and it was found to have indicator properties exactly similar to the balata product, its P_H range being 5·67 - 5·9, and with silver salt

solutions its behaviour was also identical with that of the balata compound.

Dimethoxy-diphenyl-hydrobalata.

1·66 gms. balata bromide, 1 gm. ferric chloride and 6·64 gms. anisole heated together on an oil bath at 100 - 130°C. for 3 hours. Hydrobromic acid was evolved vigorously at 120 - 130°C. After cooling, 100 ccs. benzene added, the solution filtered and then run into alcohol containing hydrochloric acid. The precipitate was then filtered, redissolved in benzene and reprecipitated by pouring into petroleum ether, this being found to be the best method. The result was 2 gms. of a grey brown coloured product, M.Pt. 105 - 110°C., soluble in acetone, benzene and ethyl acetate, insoluble in alkalies, acids, alcohol, ether, petroleum ether and water, the ethyl acetate solution being fluorescent and the benzene solution weakly so.

·1000 gms. subst. gave ·0664 gms. H_2O and ·2955 gms. CO_2

·1210 gms. " " ·0829 gms. " " ·3582 gms. "

°/o Carbon	found 80·6°/o	80·72°/o	calculated from	80·8°/o
°/o Hydrogen	" 7·36°/o	7·61°/o	$[C_5H_8(C_6H_4OCH_3)_2]_x$	7·8°/o.

Molecular weights in camphor,

Concentration	1 : 5	depression 6·78°	Mol. weight	1180
"	1 : 10	" 5·88°	" "	680
"	1 : 40	" 2·72°	" "	364

Diethoxy-diphenyl-hydrobalata.

1·66 gms. balata bromide, 1 gm. ferric chloride and 6·64 gms. phenetole were heated for 3 hours at 100 - 130°C. Hydrobromic acid was evolved strongly at 120 - 130°C.: 100 ccs. benzene were added on cooling. This solution was filtered and poured into alcohol containing hydrochloric acid. The precipitate was filtered, dissolved in benzene and reprecipitated by running into petroleum ether, yielded 3 gms. of a yellow brown compound, M.Pt. 125 - 130°C., whose solubilities and fluorescence are similar to those of dimethoxy-diphenyl-hydrobalata.

·1050 gms. subst. gave ·0762 gms. H_2O and ·3192 gms. CO_2

·1000 gms. " " ·0747 gms. " " ·2989 gms. "

°/o Carbon	found 82·9°/o	81·5°/o	calculated from	81·26°/o
°/o Hydrogen	" 8·06°/o	8·3°/o	$[C_5H_8(C_6H_4 \cdot OC_2H_5)_2]_x$	8·42°/o

Molecular weights in camphor

Concentration	1 : 5	depression 5°	Mol. weight 1250
"	1 : 10	" 5·45°	" " 733
"	1 : 40	" 2·7°	" " 370

Since there are no references to the condensation products of gutta-percha bromide with anisole and phenetole, these were prepared in order to complete the series.

Dimethoxy-diphenyl-hydrogutta-percha.

Prepared in a similar manner to the corresponding balata compound yielded 2 gms. of a greenish brown coloured

product, M.Pt. 195 - 197°C., soluble in ether, benzene and ethyl acetate, insoluble in acids, alkalies and alcohol. The ethyl acetate solution is strongly fluorescent.

·1210 gms. subst. gave ·0837 gms. H_2O and ·3566 gms. CO_2

°/o Carbon found 80·35°/o Calculated from 80·8°/o

°/o Hydrogen " 7·69°/o $[C_5H_8(C_6H_4 \cdot OCH_3)_2]_x$ 7·86°/o

Molecular weight in camphor

Concentration	1 : 5	depression	4·35°	Mol. weight	1843
"	1 : 10	"	2·5°	" "	1600
"	1 : 40	"	0·9°	" "	1110

Diethoxy-diphenyl-hydrogutta-percha.

Prepared in a similar manner to the balata compound, gave 1·8 gms. greenish brown substance, M.Pt. 205 - 207°C. Soluble in ether, benzene, pyridine and ethyl acetate, insoluble in acids, alkalies, alcohol and petroleum ether. The ethyl acetate solution is strongly fluorescent.

·1000 gms. subst. gave ·0751 gms. H_2O and ·2970 gms. CO_2

°/o Carbon found 81·02°/o Calculated from 81·26°/o

°/o Hydrogen " 8·34°/o $[C_5H_8(C_6H_4OC_2H_5)_2]_x$ 8·42°/o

Molecular weight in camphor

Concentration	1 : 5	depression	4·44°	Mol. weight	1800
"	1 : 10	"	2·68°	" "	1495
"	1 : 40	"	·78°	" "	1274.

Dihydroxy-dinaphthyl-hydrobalata.

3 gms. balata bromide, 2·5 gms. anhydrous ferric chloride and 20 gms. α-naphthol heated together for 3 hours at 100 - 105°C. The reaction went quite vigorously at first and hydrobromic acid was evolved. After cooling, 200 ccs. absolute alcohol added, solution filtered, the residue dissolved in acetone and precipitated by pouring into 500 ccs. dilute hydrochloric acid. The product, purified by reprecipitation, was 3·2 gms. of a putty grey substance, M.Pt. 190 - 195°C., soluble in benzene, acetone, alkalies and ethyl acetate, insoluble in alcohol, acids and petroleum ether.

·1040 gms. subst. gave ·0572 gms. H_2O and ·3208 gms. CO_2

·1000 gms. " " ·0548 gms. " " ·3091 gms. "

°/₀ Carbon	found 84·1°/₀	84·3°/₀	Calculated from	84·7°/₀
°/₀ Hydrogen	" 6·11°/₀	6·09°/₀	$[C_5H_8(C_{10}H_6OH)_2]_x$	6·2°/₀.

Molecular weight in camphor

Concentration	1 : 5	depression 3·6°	Mol. weight	2226
"	1 : 10	" 2·88°	" "	1389
"	1 : 40	" 1·5°	" "	666

Dinitrobenzoate. 1 gm. dihydroxy-dinaphthyl-hydrobalata in 30 ccs. pyridine mixed with 4 gms. p-nitrobenzoyl chloride in 30 ccs. pyridine yielded 1·2 gms. of a dark brown coloured compound, M.Pt. 150 - 152°C., soluble in benzene, ethyl acetate, and acetone, insoluble in acids, alkalies and alcohol.

Nitrogen (Dumas) found 4·21°/$_o$ 4·27°/$_o$

Calculated from $[C_5H_8(C_{10}H_6 \cdot O \cdot CO \cdot C_6H_4 \cdot NO_2)_2]_x$ 4·3°/$_o$.

B.

Catalytic hydrogenation of Gutta-percha and Balata.

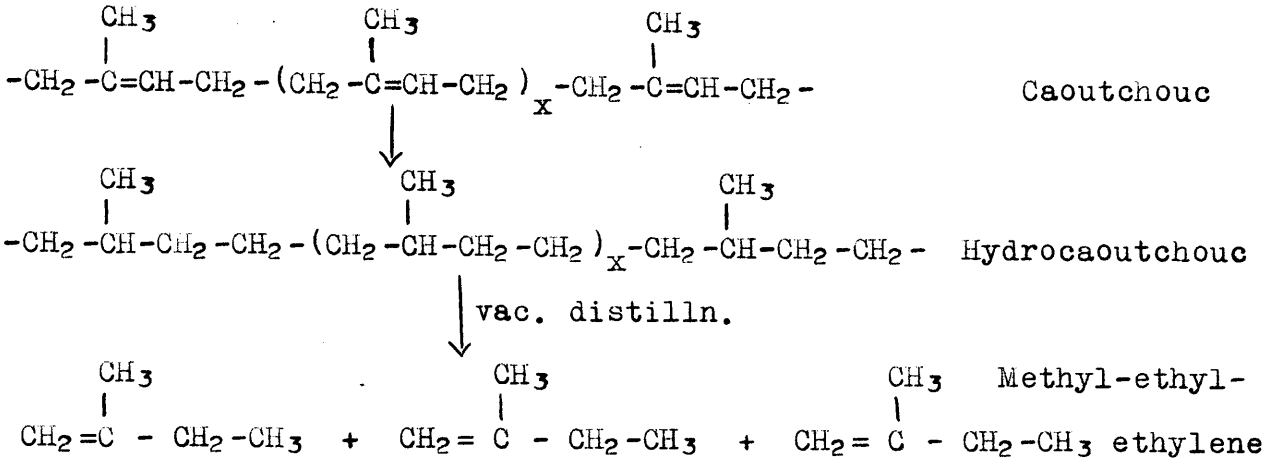
Although many chemical reactions have shown that double bonds are present in the caoutchouc, gutta-percha and balata molecules, hydrogenation, which is of the utmost importance in elucidating molecular size and for giving valuable information from distillation, has not been successfully carried out until recently.

Berthelot (Ber., 2, 33, 1869) tried to reduce caoutchouc by heating it under pressure with hydriodic acid and obtained a number of hydrocarbons boiling above 350°C., which seemed to belong to the paraffin series from their stability towards bromine and fuming nitric acid. This work has been repeated by Staudinger and Senior (Helv. C. A., 13, 1321, 1930) who find that first a degradation of the molecule takes place depending on the temperature, and then a cyclic formation due to the acid along with a reduction of the cyclic product. The resulting compound has a higher carbon and lower hydrogen content than the theoretical for hydrocaoutchouc, thus it is not a high molecular paraffin but a hemi-colloid reduction product of a cyclocaoutchouc and can give no conclusions as to the constitution of caoutchouc.

The catalytic hydrogenation of caoutchouc had been tried many times without success when, in 1922, Pummerer and Burkard (Ber., 55, 3458, 1922) and Staudinger and Fritschi (Helv. C. A., 5, 785, 1922) independently published their results. Pummerer and Burkard, using very dilute solutions of caoutchouc and platinum black activated by oxygen as catalyst, obtained hydrocaoutchouc $(C_5H_{10})_x$ in the cold or at 70 - 80°C. as a colourless, ether soluble, inelastic substance sensitive to air oxidation. Later Pummerer and Koch (Ann., 438, 294, 1924) repeated the work using very pure caoutchouc with a large excess of catalyst and obtained an opaque, tough, non-elastic mass, showing a tendency to crystallise, and the sensitivity to air was shown to be due to traces of platinum black by Pummerer, Nielsen and Gündel (Ber., 60, 2167, 1927). The hydrocaoutchouc is stable to bromine and potassium permanganate and after heating in an inert atmosphere gives a molecular weight of 1700 in camphor. Vacuum distillation did not decompose the hydrocaoutchouc and the distillate was $C_{50}H_{100}$ or $C_{50}H_{102}$ of molecular weight 714 in camphor: it was stable to bromine and potassium permanganate. The hydrocaoutchouc obtained in the cold hydrogenation is always about 0·3% low in hydrogen: this is due to slight cyclic formation going on at the same time as reduction. Pummerer, Nielsen and Gündel have repeated the vacuum distillation and they also find $C_{50}H_{102}$ as the product. They also refer to "abnormal" hydrogenation when the product is the result of partial cyclic

formation and partial hydrogenation. In this case the compound is stable to bromine, etc., but the percentage of hydrogen is much lower than the theoretical for $(C_5H_{10})_x$.

Staudinger and Fritschi hydrogenated caoutchouc without solvent at high temperatures 270 - 280° and high pressures 93 - 100 atmospheres with platinum black as catalyst. The product is a colourless, inelastic mass giving analyses corresponding well with $(C_5H_{10})_x$. This may be considered as a saturated hydrocarbon because the molecule is so large that $C_{5x}H_{10x}$ is practically the same as $C_{5x}H_{10x+2}$. The hydrocaoutchouc is stable to potassium permanganate and bromine: on long standing in sunlight slow substitution takes place with bromine. Vacuum distillation gives a series of unsaturated hydrocarbons of the type $(C_5H_{10})_x$, each having one double bond. The lowest boiling product is methyl-ethyl-ethylene C_5H_{10}; 24°/o of the distillate consists of C_5H_{100}, and $C_{10}H_{20}$, $C_{15}H_{30}$, $C_{40}H_{80}$ are also found. Harries (Ber., 56, 1051, 1923) raises the objection to the above work that, at the high temperature used, the product obtained might not be hydrocaoutchouc but a mixture of hydrogenated pyrogenetic decomposition products of caoutchouc. This is refuted by Staudinger since his hydrocaoutchouc is colloidal, has the properties of a paraffin hydrocarbon, and methyl-ethyl-ethylene is found on distillation. Therefore hydrogenation must have taken place before any decomposition set in.



The presence of the compound $C_{50}H_{100}$ in the distillate supports the view that caoutchouc has a very large molecular weight.

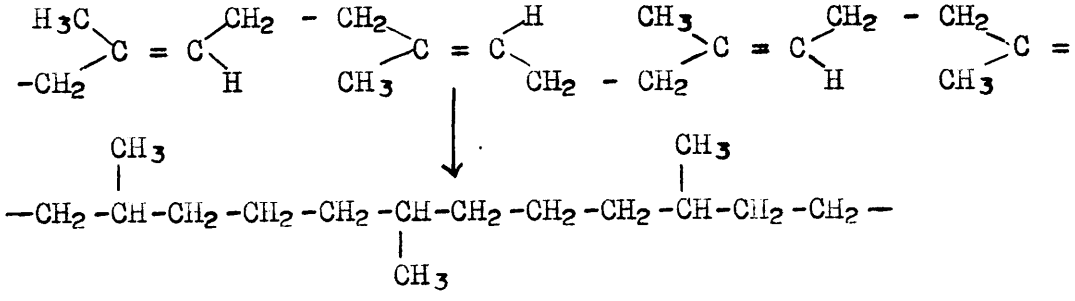
Much work on hydrocaoutchouc has been published very recently by Staudinger and his co-workers which changes to some extent the previous ideas on this subject. In a series of papers (Helv. C. A., 13, pp. 1321, 1324, 1334, 1350, 1355, 1361, 1368; 1930) the following are the chief results. Harries' original objection to the hydrocaoutchouc prepared at high temperatures and pressures is admitted and the hydrocaoutchouc so prepared is stated to be a reduction product of hemi-colloid degradation products of the original caoutchouc, internal cyclic formation also taking place. Only by cautious hydrogenation in the cold can a true hydrocaoutchouc be obtained. The complexity of the product resulting from hydrogenation at high temperatures and pressures is shown to depend on the amount and activity of the catalyst used and the temperature, a quick

hydrogenation giving a product of higher molecular weight than a slow one, and the lower the temperature the higher the molecular weight.

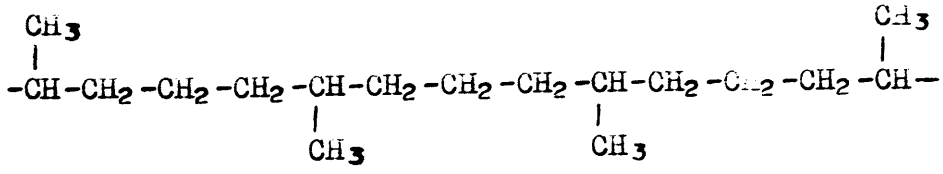
Gutta-percha and balata hydrogenated at 270°C and 100 atmospheres pressure with a nickel catalyst give products resembling hydrocaoutchouc very closely in appearance, and their refractive indices are found to be practically identical, giving the value 1·4770, thus supporting the view that on saturation of the double bonds the differences between caoutchouc, gutta-percha and balata disappear. A 1°/$_o$ solution of caoutchouc was hydrogenated in the cold using 6 gm. platinum oxide as catalyst to give a product $(C_5H_{10})_x$ of molecular weight 30,000. Reduction with platinum black took too long and reference is made to the great difficulty in freeing the cold reduction product from the catalyst. Using a 0·68°/$_o$ solution and 1·5 gms. nickel catalyst and hydrogenating at 180 - 200°C with 100 atmospheres pressure gave a product of lower molecular weight, but still much higher than that of the product of hydrogenation without a solvent.

Hydrocaoutchouc obtained by the method of Staudinger and Fritschi is a syrupy mass of molecular weight 2,000 - 10,000 which dissolves quickly in solvents to give low-viscous solutions, while hydrocaoutchouc from Pummerer and Burkard's method is a firm, somewhat elastic substance, molecular weight 20,000 -

30,000, which dissolves slowly to give very viscous solutions. Vacuum distillation according to Staudinger always results in a series of unsaturated hydrocarbons with methyl-ethyl-ethylene as lowest boiling product, and he denies Pummerer and Koch's statement that their hydrocaoutchouc distilled undecomposed to give $(C_5H_{10})_{10}$. The crystalline hydrocaoutchouc obtained by Pummerer and Koch is also severely criticised on the following grounds. On hydrogenation a more or less strong cyclic formation always occurs which results in irregularities in the molecule and so hinders crystallisation. Taking Staudinger's trans- formula for caoutchouc



it is possible that a hydrocaoutchouc might crystallise if its structure were uniform as shown, but on reduction, particularly at high temperatures, rearrangement occurs and unsymmetrical molecules are produced, e.g.,



Thus the chance of crystallisation is very remote.

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The present work was undertaken with a view to attempting the hydrogenation of gutta-percha and balata at ordinary temperatures and pressures. The hydrocarbons were specially purified by repeated precipitation with acetone from petroleum ether solution and boiling in alcohol. The catalyst used was a form of active palladium prepared by the method of Piccard and Thomas (Helv. C. A., 6, 1045, 1923) and the apparatus that described by Shaefer (Ind. Eng. Chem., p.115, 1930) to which an alteration was made later. At first chloroform was used as solvent but this was found to be unsatisfactory as it decomposed very quickly, and thereafter cyclohexane was used in all experiments. The hydrogenation was carried out in very dilute solution 0·5 to 1·3°/₀ using 1 to 2 times the weight of hydrocarbon of catalyst. The reaction was fairly slow after the first few hours and sometimes took as long as 60 hours' actual shaking: this was on occasion speeded up by the addition of fresh catalyst. The hydrogen absorption was always somewhat greater than the theoretical for $(C_5H_8)_x \longrightarrow (C_5H_{10})_x$ and part of this excess was shown by a blank experiment to be due to solution of hydrogen in the solvent and adsorption on the catalyst. The reason for the remainder is not definitely known, but this phenomenon was also noticed by Pummerer and Koch (Ann., 438, 294, 1924). Pummerer and Burkard (Ber., 55, 3458, 1922) stated that their apparatus and

measurements were so exact that an excess absorption of 10 ccs. hydrogen was held to be proof that caoutchouc consisted of a large ring or long chain system. This is now shown to be erroneous by the later publication (above) in which it is stated that an excess of 100 ccs. hydrogen may be absorbed, thus taking away the value of following the absorption by measurement. When hydrogenating a protective colloid like caoutchouc according to Paal and Gerum (Ber., 41, 805, 1908) much more than the calculated theoretical amount of hydrogen may be absorbed; accordingly Pummerer and Koch adopted the method of continuing the reduction until addition of fresh catalyst gave no further appreciable absorption. Despite this excess absorption the products did not contain more than the theoretical quantity and analysed well for $(C_5H_{10})_x$.

The solutions of the hydrogenated products showed a faint opalescence and were saturated to bromine, potassium permanganate and air at ordinary temperatures. The isolation of the hydrogutta-percha and hydrobalata was somewhat difficult as the last traces of catalyst could not be removed except by long centrifuging with kaolin or animal charcoal.

Two further varieties of catalyst were used, first, spongy palladium got by reducing a dilute solution of palladous chloride with formic acid and addition of alkali, and second, this type of catalyst precipitated on charcoal. These catalysts gave comparatively fast absorption but their removal in isolation

of the hydro-product presented such great difficulty that they were not extensively used.

The hydrogutta-percha and hydrobalata are obtained as white, tough, inelastic, waxy-looking substances soluble in the usual solvents. Analysis corresponds well with $(C_5H_{10})_x$ although the hydrogen value is very slightly low, probably indicating some cyclic formation. No instance of the so-called "abnormal" hydrogenation was encountered. The compounds give no depression of the F.Pt. of benzene, and in menthol and camphor, molecular weights by the Rast method give values of 600 - 650 and 1150 to 1250, depending on the concentration. The molecular weights are undoubtedly very high and from the appearance of the products and their solutions it is thought that they do not differ by much from those of the parent hydrocarbons. Vacuum distillation was not successful since at 2 to 3 mms. pressure, even above 360°C., only a small drop of a pale yellow distillate was obtained. This is remarkable because of (i) the much higher boiling or disintegration point of the hydro-products than that of the parent hydrocarbons, which is about 250 - 300°C., thus indicating much greater stability due to the saturation of the double bonds, and (ii) the residue in the flask showed no sign of charring or general decomposition, which also points

to exceptional stability. The distillate was found to be unsaturated to bromine, but nothing further could be done with it.

The purified gutta-percha and balata were hard, white, waxy-looking substances giving the following analyses which agree well with the theoretical,

Gutta-percha.

·1420 gms. subst. gave ·1495 gms. H_2O and ·4580 gms. CO_2

·1340 gms. " " ·1407 gms. " " ·4332 gms. "

°/₀ Carbon found 87·90; 88·20; Calculated 88·16°/₀ from $(C_5H_8)_x$

°/₀ Hydrogen " 11·70; 11·72; " 11·84°/₀

Balata.

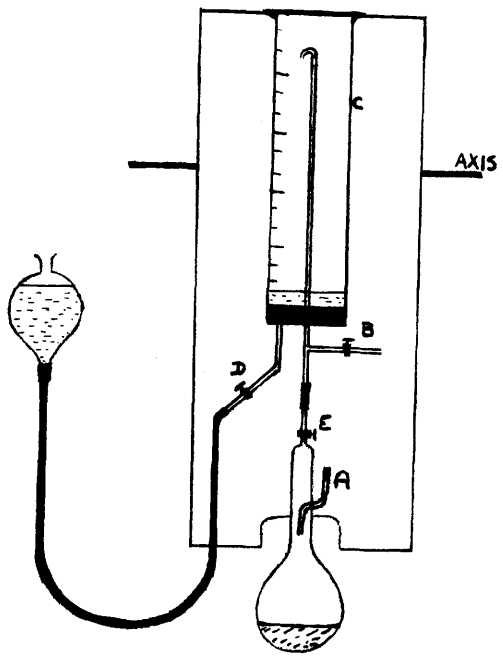
·1500 gms. subst. gave ·1590 gms. H_2O and ·4847 gms. CO_2

·1250 gms. " " ·1340 gms. " " ·4036 gms. "

°/₀ Carbon found 88·10; 88·05; Calculated 88·16°/₀ from $(C_5H_8)_x$

°/₀ Hydrogen " 11·77; 11·90; " 11·84°/₀

The apparatus first used was that described by Shaefer but it was found that on shaking, the solvent came into contact with a rubber stopper, and since the only solvents which could be used were rubber solvents, the apparatus was modified by drawing out the neck of the reaction flask and inserting a stop-cock, at the same time introducing a side arm on the flask, so that the solvent did not come into contact with any rubber.



The hydrogen was prepared from forensic zinc and 2N sulphuric acid; the gas was washed by a train of four wash-bottles (1) acid permanganate, (11) sodium hydroxide solution (111) silver sulphate solution, (1v) alkaline pyrogallate; the hydrogen being then considered quite pure. The catalyst was prepared by precipitating palladium hydroxide from dilute chloride solution with sodium carbonate. The hydroxide was then filtered, dissolved in glacial acetic acid and a stream of hydrogen passed until the palladium precipitated out. This was filtered, washed with water, dried in a vacuum desiccator

and used as required. As already stated, chloroform was useless as a solvent and cyclohexane, B.Pt. 80°C, was used in all experiments. The procedure was as follows. A weighed amount of gutta-percha or balata is dissolved in cyclohexane to give an approximate 1°/$_{o}$ solution, in an atmosphere of carbon dioxide. The required amount of catalyst, once or twice the weight of hydrocarbon, is put into the flask through the side arm A; the solution is then run in at the same opening and this side arm is then closed up. The apparatus is connected to a water-pump at B and evacuated: the stop-cock E is then opened and the whole apparatus is evacuated. It is then filled with hydrogen through B, evacuated again, and so on until it is judged that all air is removed. It is then finally filled with hydrogen and the volume read by levelling the water outside and inside the measuring cylinder. This water is previously boiled and saturated with hydrogen. The apparatus is then shaken (by a small electric motor) until no further absorption of hydrogen takes place following the addition of fresh catalyst. The following are some of the experiments carried out:-

	Weight of Hydrocarbon in gms.	% Conc. of soln. by weight.	Weight of catalyst in gms.	No. of hours shaking.	Absorption at N.T.P. in ccs.	Theoretical absorption at N.T.P. in ccs.
Gutta-	·6510	1·03	·5100	59	255	214
percha	·5000	1·09	·4600	40	193	165
	·5940	0·83	·5000	42	228	196
	·3550	0·66	1·00	36	135	117
	·4000	1·11	1·00	57	148	132
	·5650	1·24	1·00	40	215	186
	·8300	1·8	1·00	48	329	273
Balata	·4590	1·13	·5000	41	189	151
	·4000	0·55	1·00	34	147	132
	·4210	1·20	·5000	43	200	172
	·5500	1·22	·6000	42	211	181
	·3600	0·66	1·00	35	136	119
A.	·4870	1·08	1·0 + 1·5 gms. charcoal	17	185	160
B.	·4800	1·09	1·00	25	184	158

A and B are experiments using the different catalysts

referred to before. It will be seen that they are faster than the usual catalyst, but the difficulty in removing them prohibited their general use.

The hydrogen absorption readings given are corrected for solvent and catalyst absorption, since in a blank experiment 100 ccs. cyclohexane with 1 gm. catalyst absorbed 30 ccs. hydrogen. The excess absorption over the theoretical is seen to vary with the amount of hydrocarbon in the solution, but in no case is it very large.

The solutions of hydrogutta-percha and hydrobalata are faintly opalescent. They are saturated to bromine, potassium permanganate, and are not visibly changed on standing in air at room temperature. The isolation of the hydroproducts is somewhat difficult. The solution is allowed to stand until as much catalyst as possible settles: it is then filtered through a sintered glass filter, centrifuged for 1 hour, decanted, centrifuged for 2 hours with kaolin, decanted and centrifuged for a further 2 hours with animal charcoal: this is finally decanted and filtered carefully. The cyclohexane is then evaporated off in a vacuum desiccator. Hydrogutta-percha and hydrobalata are obtained as white, tough, inelastic substances, waxy to the touch. They are soluble in benzene, ether, chloroform, ethyl acetate and carbon tetrachloride, insoluble in acetone, alcohol and acetic acid. Combustion of the products gave the following results:-

Hydrogutta-percha.

·1230 gms. subst. gave ·1550 gms. H_2O and ·3870 gms. CO_2
·1160 gms. " " ·1466 hms. " " ·3640 gms. "
·1860 gms. " " ·2335 gms. " " ·5840 gms. "
·2000 gms. " " ·2550 gms. " " ·6285 gms. "

°/o Carbon found 85·78; 85·54; 85·60; 85·71; calc. 85·63
°/o Hydrogen " 14·00; 14·05; 13·95; 14·17; " 14·37

from $(C_5H_{10})_x$

Hydrobalata.

·1500 gms. subst. gave ·1885 gms. H_2O and ·4710 gms. CO_2
·1210 gms. " " ·1535 gms. " " ·3800 gms. "
·1000 gms. " " ·1254 gms. " " ·3142 gms. "
·1750 gms. " " ·2212 gms. " " ·5500 gms. "

°/o Carbon found 85·61; 85·59; 85·68; 85·70; calc. 85·63
°/o Hydrogen " 13·96; 14·1; 13·93; 14·05; " 14·37

from $(C_5H_{10})_x$

Hydrogutta-percha and hydrobalata gave no depression of the F.Pt. of benzene. Molecular weights by the Rast method in camphor and menthol were

Hydrogutta-percha

Camphor { Concentration 1 : 10 depression 6·5° molecular wt. 615
" 1 : 40 " 1·5° " " 667

Menthol { Concentration 1 : 10 depression 1·9° molecular wt. 652
" 1 : 40 " ·5° " " 620

Hydrobalata.

Camphor { Concentration 1 : 10 depression 3·5° molecular wt. 1143
" 1 : 40 " ·8° " " 1250

Menthol { Concentration 1 : 10 depression 2° molecular wt. 620
" 1 : 40 " ·5° " " 620

By this method, however, it is almost certain that either the complex molecule $(C_5H_{10})_x$ is broken down into more simple polymers, or directly decomposed, by the temperature and treatment; which alternative is correct is not clear, but the first is more reasonable and the above values may be taken to represent molecules $(C_5H_{10})_{10}$ mol. wt. 700 and $(C_5H_{10})_{20}$ mol. wt. 1400.

Neither hydrobalata nor hydrogutta-percha distilled appreciably even above 360°C at 2 - 3 mms. pressure. The distillate got in each case from 3 gms. of the hydro-product was only a small drop of a pale yellow viscous liquid which was unsaturated to dilute bromine-chloroform solution, thus indicating some slight disintegration of the products. The residue in the flask showed no sign of charring or decomposition, beyond a slight yellow colour, indicating a saturated structure.

Thus gutta-percha and balata $(C_5H_8)_x$ have been

hydrogenated at ordinary temperatures and pressures to give saturated hydrocarbons of the form $(C_5H_{10})_x$.

C.

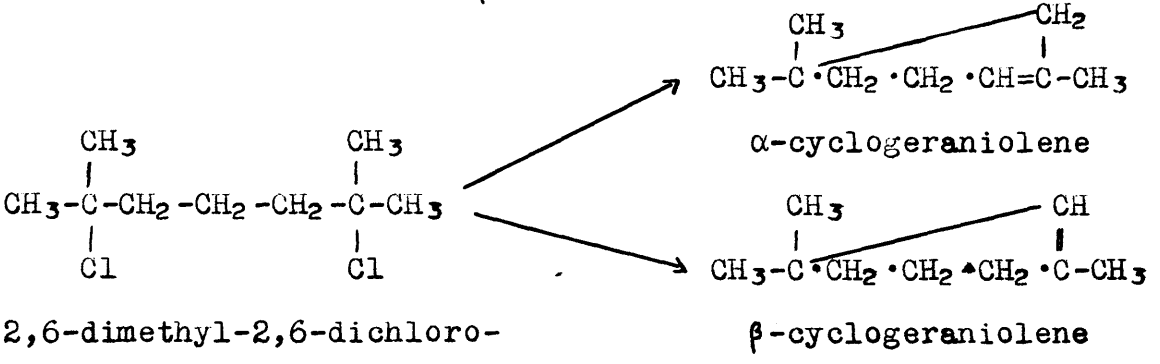
The action of Zinc Dust and Alcohol on the hydrochlorides of Gutta-percha and Balata.

In 1921 Harries and Evers (Wiss. Veröffentlich. Siemens-Konzern, 1, Heft 2, p.87, 1921; Chem. Zntr., 3, 1358, 1921; C.A., 16, 3232, 1922) believed they had obtained a partial hydrogenation of caoutchouc by the action of zinc dust on an ethylene dichloride solution of caoutchouc hydrochloride containing free hydrogen chloride. The product, a white solid of the formula $(C_{10}H_{18})_4$ and still unsaturated, was named α-hydrocaoutchouc.

Staudinger and Widmer (Helv. C.A., 9, 529, 1926), on repeating this work, found that instead of a reduction, an inner condensation or cyclic formation took place. Using zinc dust alone, the product was an incompact white substance about half as saturated as caoutchouc but still having the same empirical formula $(C_5H_8)_x$; this was named mono-cyclocaoutchouc. With zinc dust and hydrochloric acid the product was similar in appearance but had only one double bond to every 3 to 4 isoprene groups, still having, however, the same empirical formula; this was called poly-cyclocaoutchouc. The same results were obtained using caoutchouc hydrobromide instead of the hydrochloride, while other metals, e.g., iron and tin, gave similar, but impure, products, and aluminium

bronze and magnesium yielded products still rich in chlorine.

In order to form some idea as to how this cyclic formation occurs, Staudinger and Widmer studied the action of zinc dust and hydrochloric acid on mono- and dichloro-paraffins and terpenes in which the chlorine was attached to the same carbon atom as a methyl group - corresponding to the probable structure of caoutchouc hydrochloride - and found that the chlorine was always split off as hydrogen chloride. Acting on 2,6-dimethyl-2,6-dichloroheptane with zinc dust and hydrochloric acid gave α and β-cyclogeraniolene

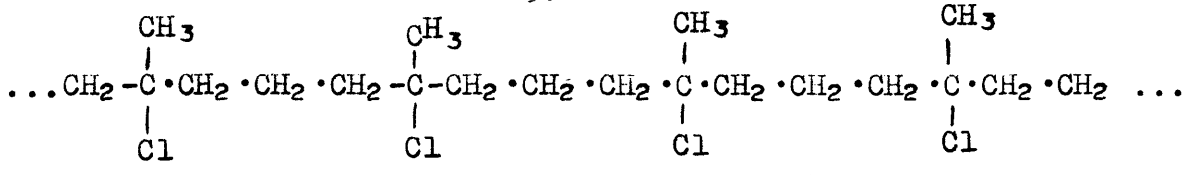


2,6-dimethyl-2,6-dichloro-heptane

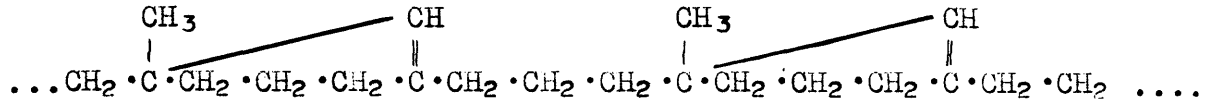
α-cyclogeraniolene

β-cyclogeraniolene

and from analogy with these results the following structures for cyclocaoutchouc were proposed,

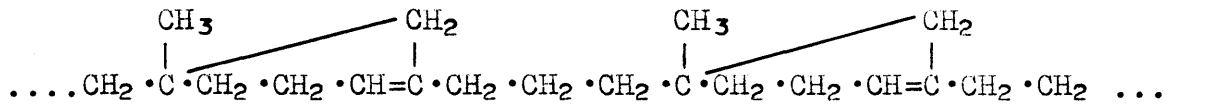


Caoutchouc hydrochloride



β-cyclocaoutchouc

or



α-cyclocaoutchouc.

These are merely meant to give a picture, however incomplete, of what possibly occurs. The formulae correspond well with mono-cyclocaoutchouc: how the further cyclic formation to give poly-cyclocaoutchouc occurs, is not known.

Mono-cyclocaoutchouc is soluble in benzene and petroleum ether, insoluble in alcohol, acetone and ether. Poly-cyclocaoutchouc is soluble in benzene, chloroform, partly in ether, and insoluble in acetone and alcohol. The substances can be hydrogenated at high temperatures and pressures to give saturated products whose hydrogen absorption corresponds to the decreased unsaturation, while ozone and potassium permanganate give oxides $(C_5H_8O)_x$ in which it appears the newly formed cycles have been broken. The action of nitric acid and sulphur mono-chloride was also observed. Density measurements show that cyclocaoutchouc is denser than caoutchouc, thus supporting the internal cyclic formation,

Caoutchouc .. 0·920

Cyclocaoutchouc 0·992

and the heats of combustion

Caoutchouc .. 10700 cals/gm.

Poly-cyclocaoutchouc 10500 cals./gm.,

confirm the fact that the cyclisation is an exothermic reaction.

Further reports of this internal cyclic formation have been supplied by Staudinger and Geiger (Helv. C. A., 9, 549, 1926), who found that on heating caoutchouc in a vacuum a cyclic formation begins about 200°C., and is rapid above 270°C. The product was a poly-cyclocaoutchouc having only one double bond to every five isoprene groups. It was a light brown powder analysing for $(C_5H_8)_x$: the density was 0·992 and the molecular weight about 2200. Poly-cyclogutta-percha has been obtained by Geiger (Ann., 468, 47, 1929) by the same method as a white powder soluble in benzene, ether and chloroform, insoluble in alcohol and acetone, and a similar product was obtained by the action of zinc dust and hydrochloric acid on gutta-percha hydrochloride. Cyclocaoutchouc and cyclogutta-percha have also been prepared by Staudinger and Bondy (Ann., 468, 1, 1929) by heating solutions of caoutchouc and gutta-percha to high temperatures.

This phenomenon has also been observed by other workers who have obtained it by various methods. Pummerer,

Nielsen and Gundel (Ber., 60, 2167, 1927) by heating caoutchouc at 90°C in 60 atmospheres of hydrogen in presence of platinum black, Fisher and Gray (Ind. Eng. Chem., 18, 414, 1926) by heating caoutchouc in sealed tubes, Fisher (Ind. Eng. Chem., 19, 1325, 1927) by the action of organic sulphonyl chlorides and acids on caoutchouc, giving products varying in hardness depending on the method of preparation, and Kirchof (Koll. Z., 30, 176, 1922) by the action of sulphuric acid on benzene solutions of caoutchouc, have all obtained products which are less saturated than caoutchouc but still have the same empirical formula. Bruson, Sebrell and Calvert (Ind. Eng. Chem., 19, 1033, 1927) obtained a product $(C_5H_8)_{10}SnCl_4$ by the action of stannic chloride on benzene solutions of caoutchouc. This dissolves in alcohol with splitting off of the stannic chloride and precipitation of the hydrocarbon as a white amorphous powder. This powder has the same composition as caoutchouc $(C_5H_8)_x$ but has no elastic properties and is less unsaturated than it, internal cyclic formation having taken place. Solution in benzene shows that this powder consists of two parts a soluble and an insoluble, in the ratio of 3 : 1 corresponding to sol- and gel-caoutchouc. Balata gave similar results, except that the cyclobalata was completely soluble in benzene.

In the present work an attempt has been made to obtain reduction products of gutta-percha and balata by the action of zinc dust and alcohol on ethylene dichloride solutions of the purified hydrochlorides since hydro-products obtained by a method other than catalytic hydrogenation would be of some interest. It was thought that the mild reducing action of zinc dust and alcohol would give the desired products, since the somewhat violent action of zinc and hydrochloric acid may have caused the cyclic formations already mentioned and since trial experiments using zinc dust alone always resulted in polymerisation. The reaction proceeds smoothly and the products, isolated by precipitation with alcohol and careful desiccation from an ether solution, were white friable powders totally unlike the parent hydrocarbons in appearance. Analysis, however, showed that no reduction had taken place, the results indicating the composition $(C_5H_8)_x$ and cyclic formation, immediately suspected, was confirmed by determination of the unsaturation which was approximately 50°/o that of the original hydrocarbon. The products are thus mono-cyclo-gutta-percha and mono-cyclo-balata analogous to the mono-cyclo-caoutchouc obtained by Staudinger. They are soluble in ether, chloroform, carbon tetrachloride and benzene, very slightly soluble in petroleum ether, and insoluble in acetone, alcohol and acetic acid. Density measurements also gave confirmatory evidence of cyclic formation. The cyclo-products give much

higher values than the parent hydrocarbon. Mono-cyclogutta-percha and mono-cyclobalata gave no depression of the F.Pt. of benzene, but molecular weight determinations by the Rast method, using camphor, gave values 2000 - 4000. Since these substances are much more soluble than gutta-percha and balata and give mobile solutions even at fairly high concentrations, it might be deduced that they are of lower molecular weight than the parent hydrocarbons. Whether this is the case or not, is not definitely known, but the molecular weights in camphor, unreliable as results from this method may be, seem to indicate this.

In each experiment a very small quantity of the product was insoluble in ether, usually about $\frac{1}{10}$ to $\frac{1}{20}$ of the soluble part. This substance showed the same composition $(C_5H_8)_x$ on analysis and the same approximate unsaturation and so is another mono-cyclo-product. The ether soluble substances may be called α-mono-cyclogutta-percha and α-mono-cyclobalata and the ether insoluble β-mono-cyclo-gutta-percha and β-mono-cyclobalata. These names are not meant to indicate that the compounds have the α- and β-structures suggested by Staudinger, but nevertheless there is a possibility that this is the case.

The α-mono-cyclo-products did not distil appreciably at 360°C and 2 - 3 mms. pressure, indicating greater stability

than gutta-percha and balata due to the cyclic formation, the result being a further cyclic formation to poly-cyclo-products as shown by the unsaturation which was about 26°/₀. The compounds could not be hydrogenated at ordinary temperatures and pressures, but the hydrochlorides and bromides were prepared. These are very similar in appearance to the corresponding compounds of gutta-percha and balata, the bromides, however, being somewhat unstable.

The hydrocarbons were purified by the usual method and the hydrochlorides were prepared as follows. 10 gms. hydrocarbon dissolved in 300 ccs. chloroform and 25 ccs. glacial acetic acid added. Hydrochloric acid gas was then passed through the solution for 24 hours when it was saturated with acid. It may be noted that passing the hydrochloric acid gas causes a marked reduction in the viscosity of the solution. Removing the excess hydrochloric acid by drawing a stream of air through the solution was found to give much purer products on precipitation with acetone. The product thus obtained by running the acid free solution in a thin stream into a large volume of acetone with rapid stirring consisted of white powdery flakes, the yield being almost quantitative, usually about 12 gms. or 85°/₀. The zinc dust was purified by leaching with very dilute ammonia solution and then dried and kept in a desiccator.

20 gms. gutta-percha hydrochloride obtained as above were dissolved in 400 ccs. ethylene dichloride to give a very dark brown, viscous solution. To this were added 75 ccs.

absolute alcohol and 10 gms. zinc dust. The solution was then refluxed on the water-bath in an atmosphere of carbon dioxide and after about 8 hours the solution was markedly lighter in colour and much less viscous. No evolution of hydrochloric acid gas took place. The refluxing was continued with small additions of zinc dust until a sample showed that the product contained no chlorine. By this time, about 8 days, the solution was very mobile and coloured only a very faint yellow. The zinc dust and zinc chloride formed were then filtered off and the solution concentrated by distilling some of the ethylene dichloride and alcohol under reduced pressure, the temperature of the water-bath being kept about 40°C. The concentrated solution was then run into a large volume of absolute alcohol at 0°C with very rapid stirring. This gave a sticky clot which was then dissolved in ether, a very small portion remaining insoluble, B. The ether solution, A, was then evaporated to dryness in small quantities in a vacuum desiccator to give finally 11 gms. of a white, friable powder, totally unlike gutta-percha in appearance. The ether insoluble portion, B, when dried gave ·5 gms. of faintly yellow, amorphous powder. This preparation was repeated twice with different quantities and the same results were obtained in each case, the proportion A to B being practically the same. Combustion of the products gave the following results:-

A.

·1200 gms. subst. gave ·1254 gms. H_2O and ·3874 gms. CO_2

·1450 gms. " " ·1506 gms. " " ·4675 gms. "

°/₀ Carbon found 88·00; 87·93; calc. 88·16 from $(C_5H_8)_x$

°/₀ Hydrogen " 11·61; 11·65; " 11·84

B.

·1000 gms. subst. gave ·1046 gms. H_2O and ·3224 gms. CO_2

·1800 gms. " " ·1880 gms. " " ·5805 gms. "

°/₀ Carbon found 87·91; 87·94; calc. 88·16 from $(C_5H_8)_x$

°/₀ Hydrogen " 11·62; 11·60; " 11·84

It is seen from these results that the expected reduction has not taken place, and to find if cyclic formation had occurred, the unsaturation was measured. This was done by titrating a dilute chloroform solution of the produce with a 1°/₀ solution of bromine in chloroform, excess bromine being added and the temperature kept at 0°C. After standing for 5 minutes excess of a concentrated aqueous solution of potassium iodide was added, the mixture well shaken, and the liberated iodine titrated with standard sodium thiosulphate using starch as indicator. Then 10 ccs. of a solution of potassium iodate were added and the liberated iodine again titrated with standard sodium thiosulphate. The first titer gives the unsaturation of the compound from the bromine addition; the second is a

correction for the amount of bromine used in substitution. The following are the results with compounds A and B.

A.

1) ·7435 gms subst. used ·9252 gms bromine by additn. and ·0971 gms by substitutn.
2) ·7435 gms " " ·9188 gms " " " " ·0727 gms. "
3) ·9726 gms " " 1·2911 gms " " " " ·1201 gms. "
4) ·9726 gms " " 1·2991 gms " " " " ·1140 gms. "

(1) 47·35°/₀ unsaturation; 5·55°/₀ by substitution.
(2) 48·34°/₀ " 4·16°/₀ " "
(3) 51·16°/₀ " 5·24°/₀ " "
(4) 51·42°/₀ " 4·98°/₀ " "

B.

1) ·1300 gms subst. used ·1642 gms bromine by additn. and ·0130 gms by substitution.
2) ·1300 gms. " " ·1642 gms " " " " ·0122 gms "

(1) 49·45°/₀ unsaturation; 4·25°/₀ by substitution
(2) 49·71°/₀ " 3·99°/₀ " "

Thus A and B are seen to be approximately half as saturated as gutta-percha itself, i.e., they have one double bond to every two isoprene groups instead of to every one. They are therefore cyclic compounds and may be called mono-cyclogutta-percha corresponding to mono-cyclocaoutchouc. The only difference between A and B is the solubility in ether: A will be named α-mono-cyclogutta-percha and B, β-mono-cyclogutta-percha.

α and β are soluble in chloroform, benzene, carbon tetrachloride, slightly soluble in petroleum ether, and insoluble in alcohol, acetone and acetic acid. α-mono-cyclogutta-percha softens at 70°C and melts to a clear amber liquid at 85 - 90°C: at 120°C it decomposes to a brown substance. β-mono-cyclogutta-percha softens about 65 - 68°C., melts at 84 - 86°C., and decomposes at 120°C.

Balata hydrochloride prepared in a similar manner and submitted to the same treatment gave exactly similar results. α-mono-cyclobalata is a white, friable powder having the same solubilities as the gutta-percha compound and melting at 100 - 105°C., decomposing at 120 - 125°C. β-mono-cyclobalata is an amorphous pale yellow powder softening at 85 - 90°C., melting at about 100°C., and decomposing at 115 - 120°C. Combustion and unsaturation determinations give the following results:-

<u>α-mono-cyclobalata.</u>

·2100 gms. subst. gave ·2216 gms. H_2O and ·6780 gms. CO_2

·1560 gms. " " ·1642 gms. " " ·5030 gms. "

°/₀ Carbon found 88·05; 87·98; calc. 88·16 from $(C_5H_8)_x$

°/₀ Hydrogen " 11·71; 11·69; " 11·84

<u>β-mono-cyclobalata.</u>

·1450 gms. subst. gave ·1527 gms. H_2O and ·4680 gms. CO_2

·1600 gms. " " ·1690 gms. " " ·5160 gms. "

°/₀ Carbon found 87·96; 87·97; calc. 88·16 from $(C_5H_8)_x$

°/₀ Hydrogen " 11·70; 11·74; " 11·84

α-mono-cyclobalata.

(1) ·1950 gms subst. used ·2259 gms bromine by additn. and ·0145 gms by substitution.
(2) ·1230 gms " " ·1521 gms " " " " ·0141 gms "

(1) 46·1°/₀ unsaturation; 5°/₀ by substitution.
(2) 47·7°/₀ " 4·6°/₀ " "

β-mono-cyclobalata.

(1) ·5810 gms subst. used ·707 gms bromine by additn. and ·0500 gms by substitution
(2) ·5810 gms " " ·705 gms " " " " ·0540 gms " .

(1) 48·04°/₀ unsaturation; 3·66°/₀ by substitution.
(2) 47·65°/₀ " 3·95°/₀ " "

Density measurements confirm the cyclic formation since the densities are much higher than those of the hydrocarbons,

α-mono-cyclogutta-percha 0·9965 α-monocyclobalata 1·0030
gutta-percha ... ... 0·920 balata ... ... 0·920

These densities were measured in absolute alcohol at 19°C, when the density of the alcohol is 0·7901.

Molecular weight determinations in camphor gave the following results:-

α-mono-cyclogutta-percha

Concentration	1 : 5	depression	2°	molecular wt.	4000
"	1 : 10	"	·95°	" "	4200
"	1 : 40	"	·65°	" "	1550

α-monocyclobalata.

Concentration	1 : 5	depression	2·1°	molecular wt.	3723
"	1 : 10	"	1°	" "	4000
"	1 : 40	"	·5°	" "	2000

β-mono-cyclogutta-percha.

Concentration	1 : 5	depression	2·2°	molecular wt.	3640
"	1 : 10	"	1·8°	" "	2200
"	1 : 40	"	·55°	" "	1800

β-mono-cyclobalata.

Concentration	1 : 5	depression	2·4°	molecular wt.	3300
"	1 : 10	"	2·05°	" "	1950
"	1 : 40	"	·52°	" "	1940

None of these compounds gave any depression of the freezing point of benzene.

In an attempted vacuum distillation 4·5 gms. α-mono-cyclogutta-percha were heated at 2 - 3 mms. pressure using a fusible metal bath. When the bath temperature reached 150°C the solid melted and bubbled furiously, and at 180°C had set to a shiny brown porous mass, which did not change even above 360°C. A very small distillate was obtained in a solid carbon dioxide trap which consisted of about 2 ccs. of a light yellow coloured liquid and 1cc. of a dark brown coloured liquid. These had a strong resinous smell and were unsaturated to bromine.

The residue in the flask weighed 3·7630 gms. and consisted of a brown, friable powder. Measurement of the unsaturation gave the following result:-

·2990 gms. subst. used ·176 gms. bromine by addition

$^{\circ}/_{o}$ unsaturation = 25·03$^{\circ}/_{o}$

This indicates that the melting and bubbling at 150°C was probably a further cyclic formation. α-mono-cyclobalata gave similar results, the refractive indices at 12° of the two liquids from the distillation being 1·3786 for the yellow liquid and 1·5155 for the brown. The unsaturation value of the residue was 24·5$^{\circ}/_{o}$.

1·590 gms. α-mono-cyclogutta-percha in 80 ccs. benzene with 1 gm. active palladium as catalyst were shaken with hydrogen at ordinary temperatures and pressures for 100 hours, but the absorption of hydrogen even then was only about 106 ccs., while the theoretical absorption was 262 ccs. α-mono-cyclobalata could not be hydrogenated either.

The hydrochlorides and bromides of α-mono-cyclogutta-percha and α-mono-cyclobalata were prepared by the same methods as the hydrochlorides and bromides of the parent hydrocarbons to which they are very similar in appearance, the cyclo-bromides, however, being somewhat unstable. Comparisons of the densities of these substances show that the cyclic formation is not broken down by the addition of hydrochloric acid or bromine. Densities measured at 19° in absolute

alcohol were as follows:-

Gutta-percha hydrochloride = ·9610; Balata hydrochloride = ·9645
" " bromide = ·9800; " bromide = ·9700

α-mono-cyclogutta-percha hydrochloride = 1·0400
" " " " bromide = 1·0700

α-mono-cyclobalata hydrochloride = 1·0550
" " " bromide = 1·0710.

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